00034100

Digitized with financial assistance from the
Government of Maharashtra
on 23 March, 2016

46

A MANUAL

OF

OTOGRAPHIC CHEMISTRY,

INCLUDING THE

PRACTICE OF THE COLLODION PROCESS

3·4100
(1. e

BY

T. FREDERICK HARDWICH,

DEMONSTRATOR OF CHEMISTRY IN KING'S COLLEGE, LONDON.

LONDON:

JOHN CHURCHILL, NEW BURLINGTON STREET.

MDCCCLV. 1855

777.5
Har/Man
'00

PRINTED BY
JOHN EDWARD TAYLOR, LITTLE QUEEN STREET,
LINCOLN'S INN FIELDS.

PH

PREFACE.

IONGST the variety of Photographic Works which have peared in this country, I am not aware of any which has r its professed object to treat of the *Chemistry* of that icnce. It is true that we have as yet much to learn in s department, and that our knowledge of the chemical ges produced by Light is confessedly imperfect; still are important facts which have been clearly ascer-l, and, it is thought, in sufficient number to form, if rly stated, the subject of a useful volume.

r object throughout the present Work has been to the style as elementary as possible, in order that it t be more adapted to the comprehension of one iously unacquainted with Chemistry. This however l not be done without giving a general sketch of the JO of chemical combination, the principles of nomen-ire, etc.; hence a division of that kind has been

adopted, and is placed, for convenience sake, after the others, although it will be more advantageous to read it either before or in conjunction with them.

In collecting materials, I have availed myself of much valuable information derived from papers published in the Journal of the Photographic Society,—from the pages of 'Notes and Queries,' and from manuals of Photography and of the Collodion Process, recently issued. I have received also great assistance from the personal kindness of friends, amongst whom I may mention, in particular, Mr. E. A. Hadow, of Bristol, Mr. Fenton, Hon. Secretary of the Photographic Society, and Messrs. Henry and Julius Pollock. Likewise I am indebted to Mr. Sparling for [illegible] peating many of my experiments upon a larger scale, a[illegible] carefully chronicling the results.

The Chapters upon Photographic Printing will, I [illegible] lieve, be found to contain much original matter, and [illegible] more minute directions for the practical carrying out [illegible] the process than have as yet appeared in print.

The subject of Collodio-Iodide of Silver is treated very fully, and includes the results of a large number of experiments, conducted with absolutely pure chemicals and under varying conditions. Mr. Hadow's researches upon Collodion, lately published in the Journal of the Chemical Society, have explained much that was obscure in the chemistry of Pyroxyline, and suggested more certain formulæ for its preparation.

Har/Man
34100

CONTENTS.

PART I.

THE SCIENCE OF PHOTOGRAPHY.

Page

INTRODUCTION 1

CHAPTER I.

HISTORICAL SKETCH OF PHOTOGRAPHY 8

CHAPTER II.

CHEMISTRY OF THE SALTS OF SILVER EMPLOYED IN PHOTOGRAPHY.

The Preparation and principal properties of the Nitrate of Silver —of the Chloride, Bromide, and Iodide of Silver.—The Solvents for the so-called insoluble Salts of Silver . . . 14

CHAPTER III.

THE PHOTOGRAPHIC ACTION OF THE SALTS OF SILVER.

Section I.—*Phenomena of the Reduction of Silver Salts by Light.*—Reduction of the Nitrate of Silver—of the Chloride, Bromide, and Iodide of Silver.—Nature of the change which takes place 24

Section II.—*The Preparation of Sensitive Surfaces.*—Points of similarity in the various Photographic processes as

Page

regards the nature of the sensitive surface.—Mode of preparing a layer of Chloride of Silver upon paper.—Simple experiments illustrating the action of Light upon Chloride of Silver—the superficial character of the decomposition 28

CHAPTER IV.

ON THE DEVELOPMENT OF AN INVISIBLE IMAGE BY MEANS OF A REDUCING AGENT.

Section I.—*General nature of the Reduction of Metallic Oxides* 37

Section II.—*Chemistry of the substances employed as reducing agents.*—Gallic Acid.—Pyrogallic Acid.—The Protosalts of Iron . . . . . 39.

Section III.—*The Reduction of the Salts of Silver by Developing Agents.*—Reduction of Oxide of Silver—of Nitrate and Acetate—of Chloride, Bromide, and Iodide of Silver.—The action of Light as favouring reduction by a Developer.—The various Colours presented by Metallic Silver in a state of fine division 42

CHAPTER V.

ON "FIXING" THE PHOTOGRAPHIC IMAGE.

Nature of the various substances which may be employed as Fixing Agents—Ammonia, Alkaline Chlorides, Bromides, and Iodides—Hyposulphite of Soda—Cyanide of Potassium 50

CHAPTER VI.

ON THE NATURE AND PROPERTIES OF LIGHT.

Section I.—*The Compound Nature of Light.*—Its decomposition into elementary coloured rays.—Division of these rays into Luminous, Heat-producing, and Chemical Rays.—Illustrations of the practical importance of such a distinction 57

Page

Section II.—*The Refraction of Light.*—Phenomena of simple refraction by parallel and inclined surfaces.—Refraction from curved surfaces.—The various forms of Lenses.—The Decomposition of white Light by Prisms and Lenses explained.—The Foci of Lenses.—Formation of a Luminous Image by a Lens 63

Section III.—*The Photographic Camera.*—Its simplest form.—The field of the Camera.—Chromatic aberration—Spherical aberration.—The use of Stops.—The double, or Portrait combination of Lenses.—Variation between the Visual and Chemical Foci in Lenses 70

CHAPTER VII.

ON THE CHEMISTRY OF THE COLLODIO-IODIDE OF SILVER.

Section I.—*Plain Collodion.*—Chemistry of Pyroxyline.—Physical properties of its solution in Ether and Alcohol, or Collodion, properly so called 83

Section II.—*Iodized Collodion.*—Sketch of the Iodides commonly employed.—Changes in Iodized Collodion by keeping 96

Section III.—*The Nitrate Bath.*—Its solvent action on Iodide of Silver.—The Changes it experiences on exposure to Light.—Acidity of the Nitrate Bath.—Alkalinity of the Nitrate Bath 101

Section IV.—*The Collodio-Iodide Film complete.*—Its physical characters modified by the amount of Iodide of Silver it contains—also by the time allowed to elapse before, and during, immersion in the Bath.—Characteristics of a perfect film of Collodio-Iodide of Silver 106

CHAPTER VIII.

ON THE PHOTOGRAPHIC PROPERTIES OF THE COLLODIO-IODIDE OF SILVER.

Section I.—*Causes which influence its Sensitiveness to Light.*—The relative proportions of Ether and Alcohol in the Collodion.—An acid condition of the Film.—Free Nitrate of

Page

Silver in contact with the particles of Iodide of Silver.—The amount of Iodide of Silver present.—The addition of bodies in a state of change and tending to absorb Oxygen.—Depression of temperature and other causes not yet thoroughly explained 111

Section II.—*Conditions affecting the Development of the latent Image.*—Presence of free Nitrate of Silver.—Energy of reducing agent.—Addition of free acid.—Presence of Nitrite or Oxide of Silver in the Film.—Temperature of the solutions 118

Section III.—*Hypotheses on the nature of the Change produced on Iodide of Silver by the action of Light* 123

Section IV.—*On the most probable Causes of the superior Sensitiveness of the Collodio-Iodide of Silver.*—Mechanical Causes.—Chemical Causes 127

Section V.—*The Gradation of Tone in Collodion Photographs, with some of the circumstances which affect it.*—The structure of film which is found to succeed best under chemically neutral conditions.—A further addition of Iodide required if powerful retarding causes are in operation.—The gradation of tone often injuriously affected by using accelerators 129

Section VI.—*On the "Fogging" of Collodion plates.*—Caused by irregularity in the Action of the Light—by Impurity of the Chemicals.—The remedies which are commonly employed for "Fogging" 135

CHAPTER IX.

ON POSITIVE AND NEGATIVE COLLODION PHOTOGRAPHS.

Definition of the terms Positive and Negative.—The same Photograph capable of representing both varieties . . . 138

Section I.—*On Collodion Positives.*—The proper time of exposure to Light.—The structure of film best adapted for Positives.—Modification of the Developer in order to brighten the Image.—Peculiarities of Pyrogallic Acid, and the Protosalts of Iron employed to develope Collodion Positives.—The Purity of the Tint affected by Oxide and

Page

Nitrite of Silver in the film.—Processes for whitening Glass Positives by a subsequent chemical action independent of the development 141

Section II.—*On Collodion Negatives.*—The exposure to light.—The structure of film best adapted for Negatives.—The means by which the intensity is increased.—The colour of Negatives, as influencing their opacity to chemical rays of light.—Peculiarities of Pyrogallic Acid and the Protosalts of Iron employed to develope Negatives.—Conversion of finished Positives into Negatives 150

CHAPTER X.

ON THE THEORY OF POSITIVE PRINTING.

The changes involved in the Printing process briefly sketched 158

Section I.—*The Chemistry of the Fixing and Colouring Bath.*—Explanation of the milkiness produced by adding acid to Hyposulphite of Soda.—The properties and preparation of the Polythionic Acids and their salts.—The chemistry of Hyposulphite of Silver.—Composition of the fixing and colouring Bath in its complete state 160

Section II.—*The Photographic Action of the Fixing and Colouring Bath.*—The ordinary phenomena of colouring a Positive proof.—The circumstances which affect the rapidity and perfection of the process.—Hypotheses on the nature of the change which takes place.—Explanation of the manner in which the efficiency of the Bath is maintained by the simple immersion of proofs.—On the use of Chloride of Gold in preparing a colouring Bath.—On a peculiar effect produced by alkaline Iodides in the Bath.—On colouring by means of Hyposulphurous Acid 172

Section III.—*Preparation of the Sensitive Paper.*—The ultimate colour of the proof affected by the degree of reduction of the surface—also by the proportions of Chloride of Sodium and Nitrate of Silver used in sensitizing.—On the use of Ammonio-Nitrate of Silver—of organic matters, Albumen and Gelatine 184

CHAPTER XI.

ON THE PROPOSED SUBSTITUTION OF BROMIDES FOR IODIDES IN PHOTOGRAPHIC PROCESSES.

Page

The relative sensitiveness of Bromide and Iodide of Silver to white Light, examined.—Superior sensibility of the former to coloured Light.—Division of the chemical rays of Light into two classes, by means of Sulphate of Quinine.—Mode in which coloured objects are copied upon Iodide of Silver 191

CHAPTER XII.

ON THE CHEMISTRY OF THE DAGUERREOTYPE PROCESS.

The nature of the Daguerreotype sensitive film.—The means by which the latent image is developed.—The strengthening of the image by means of Hyposulphite of Gold 197

PART II.

PRACTICAL DETAILS OF THE COLLODION PROCESS.

CHAPTER I.

PREPARATION OF THE MATERIALS REQUIRED IN THE COLLODION PROCESS.

Section I.—*The Collodion.*—Preparation of soluble Pyroxyline by the mixed acids, and the Nitre process.—Purification of the Ether and Alcohol.—Preparation of the iodizing compounds in a state of purity 207

Section II.—*The Nitrate Bath.*—Saturation of the Bath with Iodide of Silver and removal of free Nitric Acid.—Directions for converting a portion of the Nitrate into Acetate of Silver.—Preparation of standard solutions of acid and alkali 225

Section III.—*The developing Liquids.*—Preparation of the Protonitrate of Iron 230

CHAPTER II.

FORMULÆ FOR SOLUTIONS REQUIRED FOR COLLODION PHOTOGRAPHS.

Page

Section I.—*Formulæ for direct Positive solutions.*—Two processes described—a Sensitive process for portraits, and the Positive process usually followed.—The Collodion, Nitrate Bath, developing fluids and fixing liquids required for each.—Archer's Bichloride of Mercury whitening solution 232

Section II.—*Formulæ for Negative solutions.*—A sensitive Negative process, with neutral films.—The ordinary Negative process with dense films employed faintly acid.—The Collodion, Nitrate Bath, developing and fixing liquids required for each 242

CHAPTER III.

MANIPULATIONS OF THE COLLODION PROCESS.

Cleaning the glass plates—coating them with Collodio-iodide of Silver.—The exposure in the Camera.—Developing the image—fixing the image 249

CHAPTER IV.

CLASSIFICATION OF IMPERFECTIONS IN COLLODION PHOTOGRAPHS, WITH DIRECTIONS FOR THEIR REMOVAL.

Section I.—*Imperfections common to Negatives and Positives.*—Fogging—specks—transparent and opaque spots—markings of all kinds 265

Section II.—*Imperfections peculiar to Negatives.*—Appearance of Negatives which have been over- or under-exposed.—Imperfectly developed Negatives 272

Section III.—*Imperfections peculiar to Positives.*—Effects of over-exposure—of excess of Nitric Acid in the film, etc. 273

CHAPTER V.

THE DETAILS OF PHOTOGRAPHIC PRINTING.

Section I.—*The Preparation of the Sensitive paper.*—Selection

Page

of the paper.—Albumen paper.—Gelatine, and Ammonio-Nitrate paper 276

Section II.—*Preparation of the fixing and colouring solutions.*—Mode of preparing a colouring Bath with Perchloride of Iron—with Iodine—with Chloride of Gold.—General remarks upon the management of the fixing and colouring Baths 283

Section III.—*Manipulations of Photographic Printing.*—The exposure to light.—The fixing and colouring—the washing, drying, and mounting of the proof 289

CHAPTER VI.

ON THE MEANS OF PRESERVING THE SENSITIVENESS OF COLLODION PLATES.

The Nitrate of Magnesia process of Messrs. Crookes and Spiller.—Mr. Shadbolt's Honey process 296

PART III.

OUTLINES OF GENERAL CHEMISTRY.

CHAPTER I.

THE CHEMICAL ELEMENTS AND THEIR COMBINATIONS.

The more important Elementary Bodies, with their Symbols and Atomic Weights.—The Compounds formed by their union.—The class of Salts.—Illustrations of the nature of Chemical Affinity.—Chemical Nomenclature.—Symbolic Notation.—The Laws of Combination.—The Atomic Theory.—The Chemistry of Organic Bodies 307

CHAPTER II.

VOCABULARY OF PHOTOGRAPHIC CHEMICALS 331

A MANUAL

OF

PHOTOGRAPHIC CHEMISTRY.

INTRODUCTION.

In attempting to impart knowledge to another on any particular subject, it is not sufficient that the writer should be himself acquainted with what he professes to teach. Even supposing that to be the case, yet much of the success of his effort must always depend upon the manner in which the information is conveyed. It is important to know what to say, and *what to leave unsaid;* for as, on the one hand, a system of extreme brevity always fails of its object, so, on the other, a mere compilation of facts imperfectly explained must tend only to puzzle the reader.

Therefore it is best perhaps, if possible, to steer an intermediate course between these two extremes; that is to say, to select those points which are of fundamental and primary importance, and to enter into them with considerable minuteness, leaving others of less consequence to be dealt with after a more summary manner, or to be altogether omitted.

But independently of observations such as these, which apply to educational instruction on any subject, it may be remarked, that there are sometimes difficulties of a more

formidable description to be overcome. For instance, in treating of any science, such as that of "Photography," which may be said to be comparatively new and unexplored, how great a danger exists of erroneously attributing effects to their wrong causes! Perhaps none but he who has himself worked in the same department can estimate this point in its proper light. In an experiment where the quantities of material acted upon are infinitesimally small, and the chemical changes involved of a most refined and subtle description, it is soon discovered that the slightest variation in the usual conditions will suffice to alter the whole face of things.

Nevertheless "Photography" is truly *a science*, and the results which it yields are obtained according to fixed and unalterable laws. As our knowledge of the subject increases, we may fairly hope that all uncertainty will cease, and the same precision be attained as that with which chemical reactions are usually performed.

One means of advancing in this respect is the careful performance of accurate experiments with pure materials, and afterwards, the repetition of the same with addition of those bodies which are liable under ordinary circumstances to be met with as contaminations: no matter how they are introduced, whether purposely or otherwise, if there is a chance of their being present, the effects they produce should be noted.

All needless complexity of ingredients in the preparation of solutions, etc., ought to be avoided, and in every case the formula, if possible, reduced to its simplest expression.

If points like these are not attended to, the operator, although he may himself be at times successful in producing the most brilliant pictures, will never be able to put others in the way of doing so likewise.

The intention of the author, in writing this work, has been mainly to impart a thorough knowledge of what may be

termed the "First Principles of Photography," in order that the amateur may arm himself with a theoretical acquaintance with his subject before proceeding to the practice of it. In this way it is hoped that much loss of time and grievous disappointment from failures will be avoided.

In almost every case *a reason* will be given for the plan recommended; or, if that cannot be done, special mention of such an omission will be made.

The impurities of chemicals will be pointed out as far as is possible, and special directions given for their removal.

Amongst the variety of Photographic processes which have been devised, those only will be selected which are correct on theoretical grounds, and which are found in practice to succeed.

As the work is supposed to be addressed to one ignorant alike of Chemistry and of Photography, pains will be taken to avoid the employment of all technical terms of which an explanation has not previously been given.

SKETCH OF THE MAIN DIVISIONS TO BE ADOPTED, WITH THE PRINCIPAL SUBJECT-MATTER OF EACH.

The title given to the work is "A Manual of Photographic Chemistry,"—by which is meant, a familiar explanation of the nature of the various chemical agents employed in the Art of Photography, with the *rationale* of the manner in which they may be supposed to act.

The main division adopted is threefold:—

PART I. is the *theory* of Photographic processes minutely entered into; PART II., the *practice* of Photography upon Collodion; PART III., a simple statement of the main laws of Chemistry, and of the properties of the various substances, elementary and otherwise, with which Photographers have to deal.

PART I., or "the Science of Photography," includes a full description of the chemical action of Light upon the

various salts of Silver, and of the application of it which has been made to artistic purposes; all mention however of manipulatory details, and of quantities of ingredients, is purposely omitted.

This part is divided into twelve chapters, the principal subject-matter of which is as follows:—

Chapter I. is a sketch of the history of Photography, intended to convey to the mind a general notion of the origin and progress of the Art, without dwelling on minute particulars.

Chapter II. contains the "Chemistry" of the Salts of Silver usually employed by Photographers, with the *rationale* of the processes by which they are obtained, and their principal properties.

In Chapter III. the same subject is continued; the phenomena of the action of Light upon Silver Salts are stated, with some of the circumstances which tend to increase or diminish the effect.

Chapter IV. leads us on a step further—the production of a latent image upon a sensitive surface, and the development or bringing out to view of the same by means of chemical reagents. This, being a point of elementary importance, is carefully described; the general nature of reduction of metallic oxides, with the properties of the bodies employed to reduce, are minutely entered upon. The exact nature of the action of the Light, however, in impressing the invisible image, being more difficult of comprehension, is postponed to a future chapter.

Chapter V. is "the fixing" of Photographic impressions, so as to render them indestructible by diffused light.

Chapter VI., the *Optics* of Photography—the general nature of Light, and its decomposition into elementary coloured rays—the refraction of Light, construction of Lenses, and principles of the Photographic Camera, examined at length.

Chapters VII. and VIII. embrace a more minute description of the chemical changes involved in the highly sensitive Photographic processes upon Collodion, etc. The former of the two chapters contains an account of the "Chemistry" of all the solutions employed in the formation of a sensitive layer of Collodio-Iodide of Silver, with the physical characters of the film itself in a complete state; the latter, "the Photographic properties" of the same film, both as regards peculiarities in the action of Light and in the use of the developing agents. Great care has been expended upon the construction of these two chapters, not only in stating the facts in such a way as to render them the more easily comprehensible, but also in ascertaining, as far as could be done by systematic preliminary investigations, the exact part which each constituent of the sensitive film is called upon to fulfil.

Chapter IX. is a continuation of the subjects examined in the two previous ones; it contains the classification of Collodion Photographs under two heads, "Positives" and "Negatives," with the main differences between them; also the modifications of development, etc., required in each case, with the proper means of carrying them out.

Chapter X. treats of the production of Positive Photographs upon paper, or of prints from Negatives. The chemistry of this subject being somewhat difficult, care has been taken to simplify it as much as possible.

Chapters XI. and XII. are supplementary to the others, and a very short notice of them will suffice. Chapter XI. discusses the proposal which has been made to substitute Bromides for the Iodides, either partially or entirely, in the Photographic processes. Chapter XII. is a sketch of the theory of the "Daguerreotype," pointing out the main peculiarities of this branch of the Photographic Art, but not entering upon them at sufficient length to enable the

reader to practise the manipulatory details without further instruction.

Of PARTS II. and III. it is not necessary to say much in addition to what has already been given; their titles sufficiently explain the objects they are intended to fulfil. Attention however is particularly called to the fourth chapter of PART II., in which a classification has been attempted of the principal imperfections commonly seen in Collodion Photographs, with short directions for their removal. This chapter consists essentially of a recapitulation of facts alluded to in other parts of the work; but it is hoped that the bringing them together into a short compass may be of service.

Now on reading over such a sketch as that which is above given of the plan intended to be pursued, many perhaps will be inclined to complain that too much stress is laid upon *the Collodion process*, and that, the title of the work being of a general character, the Calotype and Albumen processes should have been included as well. In reply to this objection, the author ventures to urge that *the general theory* of every Photographic process indifferently is described, and also the properties and preparations of the chemicals concerned; the omission therefore only relates to the manipulatory details involved in those processes, which he hesitated to include simply from a feeling that it would be better not to meddle with anything with which he was not *practically* as well as theoretically acquainted.

Another objection, urged by some perhaps, may be directed against *the system of minute division* adopted throughout the work, in consequence of which it is necessarily impossible to find everything which is said upon any subject under one heading. It is true that this, as far as it goes, is a disadvantage; but it is thought that by the majority the plan of dividing and subdividing will be approved

of; and especially so, as affording an aid to the memory in recollecting facts, and also as enabling the reader to see at a glance how much he has mastered, and what remains yet to be done. The difficult points of the subject are also in that way brought before him gradually, by little and little, as he is able to learn them; whilst, by the aid of a comprehensive Index, he can review at any time all that has been said, and retrace his steps in those parts which he finds the most difficult to bear in mind.

CHAPTER I.

HISTORICAL SKETCH OF PHOTOGRAPHY.

THE Art of Photography, which has now attained to such perfection, and has become so deservedly popular amongst all classes, is one of comparatively recent introduction.

The word "Photography" means literally "writing by means of Light;" and it is taken to include all processes by which any kind of picture can be obtained in that way, without reference to the nature of the sensitive surface on which the Light is made to act.

The effects produced by Light, or those which form the basis of Photography, are *of a chemical nature;* the exposed surface is changed in properties more or less, so as to be different in certain respects from what it was before.

Now the philosophers of ancient times, although many chemical changes due to the agency of Light must have continually passed before their eyes, do not seem to have had their attention particularly directed towards them.

Some of the *Alchemists* indeed appear to have noticed the fact that a substance which they termed "Horn Silver" —and which was probably a Chloride of Silver which had undergone fusion—became *blackened* by exposure to Light; but as their ideas on all such subjects were of the most erroneous nature, nothing of consequence resulted from the discovery.

The first philosophical examination of the decomposing action of Light upon compounds containing "Silver" was made by the illustrious Scheele, no longer than three-quarters of a century ago, viz. in 1777. It was also noticed by him that some of the coloured rays of Light were more active in producing the change than others.

Earliest application of these facts to purposes of Art.—The first attempts to render the blackening of Silver Salts by Light available for artistic purposes were made by Wedgwood and Davy about A.D. 1802. The former of these chemists is better known to us from the important improvements introduced by him into the manufacture of porcelain. In conducting his Photographic experiments, a sheet of white paper or of white leather was saturated with a solution of Nitrate of Silver, and *the shadow* of the figure intended to be copied was projected upon it. Under such circumstances the part on which the shadow fell remained white, whilst the surrounding exposed parts gradually darkened under the influence of the sun's rays.

Unfortunately these and similar experiments, which appeared at the outset to promise so well, were soon checked by the experimentalists being unable to discover any means of fixing the pictures, and rendering them indestructible by diffused Light. The unchanged Silver Salt still remained in the white portions of the paper, and naturally caused the proofs to blacken all over, unless carefully preserved in the dark.

Introduction of the Camera Obscura, and other Improvements in Photography.—In the earlier experiments of Wedgwood and Davy, the objects to be copied were either laid in contact with the prepared surface, or if, from want of transparency or other obvious causes, such a plan of proceeding could not be adopted, the shadow formed by intercepting the luminous rays was employed instead.

The "Camera Obscura," or darkened chamber, by means

of which a *luminous image* of any object could be formed, was first invented by Baptista Porta, of Padua; but the intensity of light required to affect the Nitrate of Silver employed in Wedgwood's process, prevented him from making use of that instrument.

The discovery therefore of any preparation of sufficient sensibility to be influenced by the subdued light of the Camera forms an important era in the history of the Photographic Art.

In the year 1814,—that is, twelve years subsequent to the publication of Wedgwood's paper,—M. Niépce, of Chalons, directed his attention to the subject, and succeeded in perfecting a process by which pictures could be produced with the luminous image of the Camera, and afterwards fixed and rendered permanent by chemical reagents.

The sensibility of the preparations employed however, although greater than before, was still so low that an exposure in the Camera of several hours was required to produce the effect.

In the process of M. Niépce, which was termed "Heliography," or "sun-drawing," the use of the Silver Salts was altogether discarded, and in place of them a peculiar resinous substance, called Bitumen of Judæa, substituted. This resin, when smeared over the surface of a metal plate, and exposed in that way to the luminous image, became *soluble* in certain liquids, which produced no effect upon the parts of the plate kept in shadow. After subsequent treatment therefore with the solvent, which consisted of a mixture of essential oils, the *lights* of the image were represented by the metallic surface below, and *the shadows* by the unaltered resin still remaining upon the plate.

The Discoveries of M. Daguerre.—MM. Niépce and Daguerre appear at one time to have been associated together as partners, for the purpose of mutually prosecuting their researches; but it was not until after the death of

the former, that the process named the Daguerreotype was given to the world. Daguerre seems to have been dissatisfied with the slowness of action of the "Bitumen sensitive surface," and to have directed his attention mainly to the use of the Salts of Silver, which are thus again brought before our notice.

The discovery of M. Daguerre was reported in June, 1839; and in the following month a bill was passed securing to him a pension for life of 6000 francs.

Even the earlier specimens of the "Daguerreotype," although far inferior to those subsequently produced, possessed a beauty which had not been attained by any Photographs prior to that time.

The sensitive plates of Daguerre were prepared by exposing a silvered tablet to the action of the vapour of *Iodine*, in such a way as to form a layer of the Iodide of Silver upon the surface. By a short exposure in the Camera an effect of some kind was produced, not visible to the eye, but *developed* by the subsequent action of mercurial vapour.

Herein lay the great importance of Daguerre's discovery—he did not attempt to produce the image by *the direct action of Light alone.* This at best must always have been a slow and tedious process, whereas, by combining the action of Light with that of chemical reagents, the same end was accomplished in an infinitely shorter space of time; what had before taken *hours* was now effected in *minutes*, and hence the utility of the Art was greatly promoted.

Daguerre likewise succeeded in doing that which had foiled the earlier experimenters, viz. *the removal of the unaltered Silver Salts*, and the consequent "fixing" of the Photographic proofs. The processes however employed for that purpose were exceedingly imperfect, and the matter cannot be said to have been fully set at rest until the publication, in the Journal of the Royal Society, of a paper

by Sir John Herschel, on the property possessed by solutions of "Hyposulphites" in dissolving the so-called insoluble Salts of Silver.

On the Multiplication of Photographic Impressions, and other Discoveries of Mr. Fox Talbot.—The researches of Daguerre and Talbot appear to have been carried on as nearly as possible at the same time, but independently of each other.

The first communication made to the Royal Society by Mr. Fox Talbot, in January, 1839, included only the preparation of a sensitive paper for copying objects by application. Soon afterwards however pictures were exhibited obtained by aid of the Camera, the sensibility having been proportionately increased. The Talbotype or Calotype process,—the latter term being derived from two Greek words signifying *beautiful picture*—possesses the following characteristics.

The sensitive layer of Iodide of Silver is supported upon a sheet of paper, and the invisible image developed by a solution of a substance known as Gallic Acid.

The use of a surface of paper to receive the sensitive salt, in place of a metal, possessed many advantages, both on the score of economy and also of portability, but in particular this one, viz. the possibility thereby given *of multiplying the impressions ad infinitum*, without again having recourse to the Camera. This fact is explained by the *transparency* of the tissue of paper, in virtue of which the original Photograph when laid upon a second sensitive sheet, allowed the rays of light to permeate it to a certain extent, and so produced a repetition of itself in a manner the details of which will be described in a subsequent chapter.

The production of a *negative* Photograph, or "Matrix," from which any number of positive copies might be obtained, constitutes a cardinal point in Mr. Talbot's invention, and his title to it has never been disputed.

On the use of Glass Plates to retain Sensitive Films.—The principal defects in the Calotype process have always been attributable to the coarse and irregular structure of the fibre of paper, even when manufactured with the greatest care, and expressly for Photographic purposes. In consequence of this, the same amount of exquisite definition and sharpness of outline as that resulting from use of metal plates, could not be obtained.

We are indebted to Sir John Herschel for the first use *of glass plates* to receive sensitive Photographic films.

The Iodide of Silver may be retained upon the glass by means of a layer of "Albumen," or white of egg, as proposed by M. Niépce de Saint-Victor, nephew to the original discoverer of the same name.

A more important improvement still was the employment of "Collodion" on glass for a similar purpose.

The *nature* of Collodion will be more fully explained as we proceed; it is an ethereal solution of a substance akin to "Gun-cotton," which leaves behind a jelly-like mass upon evaporation. It seems that M. Le Grey of Paris originally suggested that such a substance might possibly be rendered available in Photography, but our own countryman, Mr. Archer, was the first to carry out such an idea practically. In a communication to 'The Chemist' in the autumn of 1851, this gentleman gave a description of "the Collodion process" much as it now stands; at the same time proposing the substitution of *Pyro*-gallic acid for the Gallic acid previously employed.

At that period probably no idea could have been entertained of the stimulus which this discovery would be the means of rendering to the progress of the Art; but an experience of three years has now abundantly demonstrated, that, as far as all qualities most desirable in a Photographic process are concerned, none can excel, or perhaps equal, the Collodion process.

CHAPTER II.

CHEMISTRY OF THE VARIOUS SALTS OF SILVER EMPLOYED IN PHOTOGRAPHY.

By the term "*Salt* of Silver," we understand that the compound in question contains Silver, but not in its elementary form; it is Silver combined with other bodies in a peculiar manner, so that its physical properties are completely masked. Silver is familiarly known to us as a white metal, susceptible of a brilliant metallic lustre, but *a Salt* of Silver possesses no properties whatever of that kind. If any metallic substance is present in the Salt, it is plainly associated with other elements in such a way that its original characters are not discerned.

Silver is not the only metal which forms "Salts;" there are Salts of Lead, Salts of Copper, Salts of Iron, etc. "Sugar of Lead" is a familiar instance of a Salt of Lead. This substance is a white crystalline body, easily soluble in water, the solution possessing an intensely sweet taste; chemical tests prove that it contains Lead, although no suspicion of such a fact could have been entertained from a consideration of its external properties.

"Common Salt," or Chloride of Sodium, which is the type of these bodies, also possesses a similar composition; that is to say, it contains a metallic substance, the characters of which are masked, and lie hid in the compound.

The principal Salts of Silver which are employed in the Photographic processes are four in number, viz. Nitrate of Silver, Chloride of Silver, Iodide of Silver, and Bromide of Silver.

A. CHEMISTRY OF THE NITRATE OF SILVER.

Properties of the Nitrate of Silver.—Nitrate of Silver, when pure, occurs in the form of white crystalline plates, which are very heavy, and dissolve in water with great readiness. The solution is perfectly neutral in every sense of the term, and does not change the colour of blue litmus-paper.

Sometimes the Nitrate of Silver is sold in small cylindrical sticks, which are obtained by melting the salt, and running it, whilst in the fluid state, into a mould; it is then termed "lunar caustic," being employed for cauterizing wounds, and other surgical purposes.

Preparation of Nitrate of Silver.—Nitrate of Silver is prepared by dissolving metallic Silver in *Nitric Acid* or Aquafortis. This Nitric Acid is a powerfully acid and corrosive liquid, containing two elementary bodies united together in certain proportions. These bodies are Nitrogen and Oxygen, the Oxygen being present in by far the larger quantity of the two. Nitric Acid then contains much Oxygen; but what we notice particularly now is, that this Oxygen is not only large in amount, but also *loosely combined with the other element*, that is, with the Nitrogen. If such were not the case, the Nitric Acid would not possess that extraordinary energy in dissolving metals which it is found to do. Supposing a small piece of silver foil, or a silver coin, be placed in each of two test-tubes, one of which contains Sulphuric Acid, and the other Nitric Acid; on the application of heat a violent action soon commences in the latter, but the former is unaffected. Now Sulphuric Acid, or Oil of Vitriol, is an

exceedingly powerful acid,—equally or perhaps more so in some respects than the Nitric,—and it also contains much Oxygen, but yet it does not dissolve the silver; and why? because this Oxygen is retained with great force by the Sulphur, and is not *loosely combined* with it, as it was with Nitrogen in the Nitric Acid.

Difference between "Solution" and "Chemical Combination."—In order to demonstrate to the student the importance of this difference in the two cases, it is necessary to inform him, that when any metallic substance dissolves in an acid, it does not do so in the same way that salt or sugar dissolves in water. If you take a solution of salt in water, and boil it down until the whole of the water has evaporated, you obtain the salt back again in a state no way different from what it was before; but if a similar experiment is performed with a Solution of Silver in Nitric Acid, the result is not the same: in that case you do not get *metallic Silver* on evaporation, but Silver combined with Oxygen and Nitric Acid, both of which are tightly retained, being in fact in a state of chemical combination with the metal.

This then is the distinction between "mere solution" and "chemical combination;" and the action of acids upon metals belongs to the latter class.

If then we closely examine into the effects produced by treating Silver with Nitric Acid, we shall find them to be of the following nature:—first, a certain amount of Oxygen is imparted to the metal, so as to form an "Oxide," and afterwards this Oxide dissolves in another portion of the Nitric Acid, producing *Nitrate* of the Oxide, or, as it is shortly termed, Nitrate of Silver.

We can now therefore see why it is that the Nitric Acid succeeds better than the Sulphuric in the experiment of dissolving Silver. It is essential that *Oxygen* should be yielded up to the metal before it becomes ca-

pable of solution, and the Sulphuric Acid refuses to do this. Nitrogen and Oxygen have scarcely any affinity for each other, and hence, in the compound substance—the Nitric Acid—they are held together lightly. On the other hand, Sulphur and Oxygen join more firmly, and are not so quickly forced asunder.

Nitric Acid stands high in the list of "oxidizing substances," from this fact of its instability; and the student will find, in the course of his Photographic experiments, that it is continually being brought before his notice.

Mode of obtaining the solid Nitrate from solution of the metal in Nitric Acid.—After the metallic Silver has been dissolved in Nitric Acid, in the preparation of Nitrate of Silver, the solution is boiled down nearly to dryness, in order to drive off the excess of Nitric Acid, and is then set aside to crystallize. The crystals however procured in this way are still *strongly acid to test-paper;* and this is, usually speaking, their condition when sold in the shops. By heating them carefully to a point some few degrees above the temperature of boiling water, they may be rendered perfectly neutral.

B. THE CHLORIDE OF SILVER.

Properties of Chloride of Silver.—The Chloride of Silver affords us a further illustration of the nature of Salts. It is never met with in crystals like the Nitrate, but as a soft white powder, resembling common chalk or whiting in appearance. It does not dissolve in water, and is comparatively unaffected by boiling with the strongest acids. How different in these respects from the Nitrate! and yet both are Salts of Silver: the one is an oxide of Silver combined with Nitric Acid, the other is metallic Silver combined with Chlorine.

Preparation of Chloride of Silver.—The Chloride of Silver may be prepared in two ways, which are of a very

distinct nature: the first is, by the direct action of Chlorine upon metallic Silver; the second, by double decomposition between two salts adapted for the purpose.

First plan, by direct action of Chlorine upon metallic Silver.—The properties of Chlorine Gas are more fully described in the third division of this work. It is there shown to be an elementary substance possessing most energetic chemical affinities, which affinities are principally directed *towards the metals.* Chlorine is in many respects not unlike Oxygen; and as this element combines with bodies, forming Oxides, so does Chlorine with the same bodies, forming *Chlorides.*

If a plate of polished silver be exposed to a current of Chlorine Gas, it becomes after a short time coated on the surface with a white powder, which, when it reaches a sufficient degree of thickness, can be scraped off and collected. This powder is the Chloride of Silver, and it contains the two elements Chlorine and Silver intimately united.

Second plan, by double decomposition between two Salts.—In order that any two salts when mixed together in solution should give rise to the production of Chloride of Silver, nothing more is necessary than that they should both dissolve in water, and that the one should be a salt of Silver, and the other a salt containing Chlorine. Under such circumstances we may predict for a certainty, that the Chloride of Silver will be formed; the reason being, that this salt is *insoluble in water.*

In order to illustrate a case of double decomposition resulting in the formation of Chloride of Silver, take a solution in water of the Chloride of Sodium, or common salt, and mix it with another solution containing the Nitrate of Silver; immediately a dense, curdy, white precipitate falls, which is the substance in question.

Now in this reaction, all the elements, so to speak,

change places; the Chlorine leaves the Sodium with which it was previously combined, and crosses over to the Silver; the Oxygen and Nitric Acid are released from the Silver, and unite with the Sodium; thus

Chloride of Sodium *plus* Nitrate of Silver
equals Chloride of Silver *plus* Nitrate of Soda.

This re-action is an instance of what chemists term "double decomposition," and the student will find further illustrations of the same in Part III. At present it is sufficient to remark, that only those salts which are *insoluble in water* can be prepared by double decomposition, the interchange of elements which constitutes such a process not taking place under different conditions. It has already been mentioned, that the essential requirements in two salts intended for the preparation of Chloride of Silver by this method, are simply that the first should contain *Chlorine*, the second *Silver*, and that both should be *soluble in water*; hence, the Chlorides of Potassium and Ammonium succeed equally well with the Chloride of *Sodium*, and the Sulphate or Acetate of Silver as well as the *Nitrate*.

Purification of the Chloride of Silver after the double decomposition is complete.—After the double decomposition between the two salts has properly taken place, the Chloride of Silver, as before said, sinks to the bottom; the liquid above contains the *Nitrate of Soda*, the other product of the change; and it is necessary to remove this, by pouring off and washing the white curds several times with distilled water. After this is done, the product is in a pure state, and may be dried, etc., in the usual way.

C. THE IODIDE OF SILVER.

For a description of the properties and general nature of the elementary substance "Iodine," the reader is referred to the third division of the work. As present we

observe only that it closely resembles *Chlorine* in its chemical properties; and hence, as might have been anticipated, their Silver Salts are similar also.

Properties of the Iodide of Silver.—The Iodide of Silver is a soft impalpable powder, like the Chloride; but it is different from it in colour, being of a *light straw-yellow* tint. It is also, as was the case with the Chloride, perfectly insoluble in water, and even in strong acids.

Preparation of the Iodide of Silver.—All that has been already said of the preparation of Chloride of Silver, applies essentially to the Iodide, substituting in every case the word "Iodine" for "Chlorine." Thus Iodide of Silver is prepared by the direct action of the vapour of Iodine upon metallic Silver, and also by double decomposition between the Iodide of Potassium or Sodium and the Nitrate of Silver; in both cases, the same rules apply with regard to the purification of the salt, etc., as those already given.

D. THE BROMIDE OF SILVER.

It is not intended to detain the student with an account of the properties and preparation of this salt. By reference to Part III., it will be found that the element Bromine is closely analogous both to Chlorine and Iodine; it stands on the list intermediately between the two.

The Bromide of Silver is a yellowish powder, resembling the Chloride and Iodide in its preparation and properties.

ON THE SOLUBILITY OF CHLORIDE, BROMIDE, AND IODIDE OF SILVER IN CERTAIN CHEMICAL REAGENTS.

The Nitrate of Silver, as has been shown, dissolves very readily in water, but the Chloride, Bromide, and Iodide are all exceedingly insoluble; no effect whatever is produced upon them by boiling in water, or even in the strongest Nitric Acid.

As far as Photography is concerned, it is most important, and indeed essential, that we should possess means of dissolving these salts; and hence the whole subject will be fully treated of in Chapter V., "On the Fixing of Photographic Proofs:" at present we confine ourselves to a simple enumeration of the solvents of the "insoluble" Salts of Silver.

1. *Chlorides, Bromides, and Iodides of the Alkalies.*—By the "alkaline" elements, we mean Potassium and Sodium, also Ammonium, which, although compound in its nature, reacts like an element. A *Chloride* of either of these possesses the property of dissolving a portion of Chloride, Bromide, or Iodide of Silver. An *Iodide of* an alkali does the same, so also does an alkaline *Bromide*. In all these cases it is something more than *mere solution* which takes place, and it can be shown to be so in this way: if you take a strong solution of Iodide of Potassium, and add Iodide of Silver to it, a portion of this substance dissolves, and, on evaporation, crystals are obtained, which are *compound* in their nature. They are, strictly speaking, "a double Iodide of Potassium and of Silver," and they contain both of these salts, combined together chemically.

The same remark also applies to the Chloride of Silver dissolved in an Alkaline Chloride; or to the Bromide, under similar circumstances.

2. *Ammonia* (see Part III.).—Chloride of Silver is freely soluble in the alkali Ammonia, although not so in Potash or Soda. Iodide of Silver however is not soluble in Ammonia, and in this way the two salts may easily be separated.

3. *Solution of Nitrate of Silver.*—A strong solution of Nitrate of Silver dissolves the Iodide of Silver *sparingly*. This fact does not appear to have been noticed in chemical works, previous to its discovery by practical Photographers; it will be again alluded to as we proceed.

4. *Hyposulphite of Soda.*—This is a remarkable salt, the chemistry of which is described in Part III., and also in Chapters V. and X. It is a most active solvent for all the Salts above alluded to. It will be shown, as we proceed, that the solution of the Chloride, Iodide, etc., of Silver in Hyposulphite of Soda, is strictly a case of chemical decomposition. The salts first are converted into "Hyposulphite," and then dissolved; so that the liquid really contains a Hyposulphite of Silver, and not a Chloride or Iodide of Silver as the case might be.

5. *Cyanide of Potassium.*—This salt is fully described in Chapter V. and Part III. Although it is now placed *last* upon the list of solvents, it is nevertheless perhaps more energetic than any other, even than the Hyposulphites. In this case, as before, the salts are first *decomposed*, and then dissolved; a Cyanide of Silver is formed by interchange of elements, and this Cyanide is taken up by the alkaline Cyanide.

CHAPTER III.

ON THE PHOTOGRAPHIC ACTION OF THE SALTS OF SILVER.

Besides those Salts of Silver which have just been described, there are many others well known to chemists, as, for instance, the Acetate of Silver, the Sulphate, the Oxalate, etc. Some of these are met with in crystals which are soluble in water, whilst others are pulverulent and insoluble.

As a general rule, the Salts of Silver are white, or nearly so, when first prepared, and they remain white if kept in a dark place; but they possess the remarkable peculiarity *of changing in colour and becoming black by exposure to the action of Light.*

Now the salts of other metals are not in general affected in this way: whatever may have been their colour when first prepared, such they remain, without exhibiting much tendency to change. The decomposition by Light then, with a few exceptions, is a peculiarity of the salts of Silver, and it is the foundation of all the Photographic processes in common use.

In treating this subject, the action of Light upon the various Salts of Silver will first be described; this will constitute the subject-matter of Section I. Section II. explains the theory of the preparation of a surface in a

condition the most favourable for being impressed by the luminous rays.

SECTION I.

Phenomena of Reduction of Salts of Silver by Light.

This Section is subdivided into three parts.—A. The *phenomena* of the action of Light upon the Nitrate of Silver.—B. Upon the Chloride and Iodide of Silver.—C. The nature of the change which takes place.

A. ACTION OF LIGHT UPON THE NITRATE OF SILVER.

The Nitrate of Silver is perhaps a more permanent salt than almost any other of the Silver compounds. It may be preserved unchanged in the crystalline form, or in solution in distilled water, for an indefinite length of time, even when constantly exposed to the diffused light of day.

The reason of the comparative permanence of the Nitrate of Silver, must be attributed to *the nature of the acid* with which the Oxide of Silver is associated in that salt. It will be shown hereafter, that the *Nitric* Acid tends to operate in a manner directly opposed to the effect produced by the Light; and hence the stability of the salt is maintained under circumstances which would otherwise speedily destroy it.

Conditions which accelerate or increase the Action of Light upon Nitrate of Silver.—Nitrate of Silver, although not usually speaking susceptible to the influence of Light, may be rendered so by adding to its solution in distilled water a portion of what chemists term "organic matter," that is to say, matter of vegetable or animal origin. (*Vide* Part III.)

The phenomena produced by addition of organic matter, may well be illustrated by dipping a pledget of cotton-

wool, or a sheet of white paper, in solution of Nitrate of Silver, and exposing it for a few minutes to the direct rays of the sun; it soon begins to darken, and continues to do so, until it is perfectly black.

The stains upon the skin produced by handling Nitrate of Silver are caused in the same way: the organic matter and Light operating together perform what neither of them could do separately.

The comparative permanence of the pure Nitrate of Silver has just been attributed to the protecting influence of the powerful oxidizing acid it contains; now the action of the organic matter is to neutralize this effect, and to restore the conditions more nearly to what they would be if no acid, or an acid of weaker power, were present.

Some kinds of organic matter facilitate the blackening of Nitrate of Silver more decidedly than others. Without anticipating our subject by entering at all deeply into the matter, we may observe, that the accelerating effect is usually proportioned to *the degree of attraction for Oxygen which the organic substance possesses.* As the *Nitric Acid* contained in the Salt hinders the action by tending to yield up Oxygen, so those bodies which are most ready to absorb Oxygen operate best in restoring the equilibrium.

B. ACTION OF LIGHT UPON CHLORIDE, BROMIDE, AND IODIDE OF SILVER.

These three salts are classed together, not that they are in themselves of minor importance, but because, as far as we are at present concerned, the differences between them are slight.

It has already been shown that the Nitrate of Silver is not sensitive to Light except it be combined with organic matter; and even when it is so combined, it is not

sufficiently rapid in action to be well adapted for Photographic purposes.

The Chloride, Iodide, and Bromide of Silver are all of them more sensitive preparations, but they are not seen to be so if employed in a pure and isolated state. They change, it is true, under any circumstances, but they change slowly; in this case, as before, it is necessary to make use of certain accelerating agents, if we wish to observe the characteristic effects in the most marked degree.

These accelerating conditions are as follows:—1. *The presence of moisture.* If the salts are thoroughly and completely dried by chemical means, the change in colour by action of Light does not take place, or, at all events, not to an appreciable extent.

2. *Of moisture and organic matter combined.*—The remarks already made when speaking of the Nitrate of Silver will apply equally well to the Chloride. Organic matter of all kinds produces the effect, but especially that variety of organic matter which tends to absorb Oxygen.

3. *Presence of an excess of Nitrate of Silver.*—The addition of a portion of Nitrate of Silver to the pure Chloride, Iodide, or Bromide of Silver, wonderfully accelerates the action of Light; under such circumstances the blackening commences quickly, and proceeds to a far greater extent than before. The student will understand the reason of this more perfectly when the subject is fully explained, as it will be in the next Chapter.

C. NATURE OF THE CHANGE PRODUCED BY THE DIRECT ACTION OF LIGHT UPON THE SALTS OF SILVER.

The change produced by Light upon the salts of Silver may conveniently be studied by suspending a portion of pure Chloride of Silver in distilled water, and exposing to the sun's rays for several days. When the process of

darkening has proceeded to a considerable extent, if the supernatant liquid be examined by litmus-paper, it will be found to be no longer neutral, but to have acquired an acid reaction.

On applying the proper chemical tests, the acidity is found to be due to some substance dissolved which contains *Chlorine;* but as the *Chloride of Silver* is not soluble in water, it is clear that the Chlorine must in some way have been separated from its union with that metal.

Another proof that such separation has in reality taken place, is found in the fact that the "blackened" Chloride of Silver is different in properties from the white Chloride. The latter is soluble in Hyposulphite of Soda, the former is not, and this change of properties no doubt implies a change in *composition* likewise.

Putting these two facts together,—viz. the after-presence of Chlorine in the supernatant liquid, and the change in properties of the black deposit,—we say that the effect of the Light upon the Chloride of Silver has been to remove from it either a portion or the whole of its Chlorine. The affinity of Chlorine for Silver is strong, but, in some mysterious way which we cannot comprehend, the luminous rays are enabled to destroy it.

In the same manner, if the pure Iodide of Silver be exposed for a long time to a powerful light, although it does not become black, yet it changes in properties more or less, so as to become *insoluble* in the solution before employed, viz. the Hyposulphite of Soda; the probability is, that a portion of Iodine is removed in this case, just as Chlorine was in the last.

Chemical composition of the Chloride of Silver darkened by Light.—This will, for particular reasons, be explained more at length in a subsequent chapter; at present we may say, that, usually speaking, *the whole* of the

Chlorine is not separated, but only *a portion of it*,—the darkened salt still containing Chlorine, but in less quantity than the white salt.

If we call the first a *Proto*chloride of Silver, then the second is a *Sub*chloride: thus,

Protochloride of Silver = Ag Cl.
Subchloride of Silver = Ag_2 Cl.

In this case however, as in others relating to difficult points of Photographic Chemistry, we are compelled in great measure to confess our ignorance. The compounds of Chlorine and of Iodine with metallic Silver need further investigation; and there is much reason to think that they are more numerous than is generally supposed.

SECTION II.

On the Preparation of Sensitive Surfaces.

In the performance of his earlier experiments on the decomposition of Silver Salts by Light, the student may conveniently make use of ordinary "test-tubes," in which small quantities of the two solutions necessary for the double decomposition may be mixed together.

Such a plan of proceeding however can never, from the nature of it, be available for purposes of art; since the salt, whether it be the Chloride or Iodide of Silver, is under those circumstances precipitated in a state highly unfavourable to the operation of the luminous rays. When strong solutions of Chloride or Iodide of Sodium and of Nitrate of Silver are brought into contact with each other, the insoluble Silver Salt falls to the bottom in dense and clotted masses. These clots, when exposed to the sun's rays, quickly blacken on the exterior, but the inside is perfectly protected, and remains white.

Therefore it is of the first importance, as far as Photo-

graphy is concerned, that the sensitive material should exist in the form of *a surface*, in order that the various particles of which it is composed may each one individually be brought into relation with the disturbing force.

The object of the present Section is to describe briefly the *theory* of the general methods by which *Sensitive Surfaces* are prepared; and to detail a few simple experiments illustrative of their decomposition by the chemical rays of Light.

The observations to be made may be included under the following heads:—A. Similarity of the various Photographic processes commonly employed.—B. Preparation of a sensitive layer of Chloride of Silver upon paper.—C. Simple experiments illustrative of the Action of Light upon Chloride of Silver.—D. Superficial character of the decomposition producing the darkened surface.

A. POINTS OF SIMILARITY IN THE VARIOUS PHOTOGRAPHIC PROCESSES COMMONLY EMPLOYED.

In all Photographic processes which are in common use the sensitive agent consists of either Chloride, Bromide, or Iodide of Silver.

The differences between them are to be found, not in *the nature of the material* employed to receive the luminous impression, but in *the manner in which a finely divided layer of this material is exposed to the decomposing agency.*

In the Daguerreotype the Iodide of Silver is supported upon a metallic plate.

The Talbotype, with its modifications, embraces all those processes where *paper* is used for the same purpose.

In the Albumen process a plate of glass is employed, coated on the surface with a layer of Albumen, or white of egg.

The Collodion process has a thin film of the peculiar

organic substance termed Collodion spread upon glass, and this film retains the Iodide of Silver, and prevents it from falling away and being lost.

At the present time we confine ourselves to a description of the preparation of the simplest form of sensitive surface, viz. that of a Chloride of Silver upon paper.

B. MODE OF PREPARING A SENSITIVE LAYER OF CHLORIDE OF SILVER UPON PAPER.

In the last Chapter two different methods of preparing the Chloride of Silver were described: the first, by the direct action of the Chlorine gas upon metallic Silver; the second, by double decomposition between a soluble Chloride and a soluble Silver salt.

Now the latter of these two methods, being the most convenient, is in practice universally adopted.

Two solutions are prepared—the one of Chloride of Sodium, the other of Nitrate of Silver; the strength of each being adjusted after certain general rules.

A sheet of porous paper is then partially saturated with one of these liquids, and afterwards allowed to imbibe a certain portion of the other; on coming in contact within the substance of the paper, the two solutions mutually decompose each other and produce Chloride of Silver, which lies loose and in a fine state of division amongst the fibres.

At the same time also, from the nature of the reaction, an equivalent portion of *Nitrate of Soda* is formed. This salt however, being soluble in water, is not deposited, and exercises no influence whatever upon the ultimate result.

A little reflection will show, that it is not a matter of indifference in what order the two solutions above given are applied. If the Silver were used first and the "salt" afterwards, the probability is that there would be an ultimate excess of salt upon the paper. At all events, supposing the action to be continued sufficiently long, there would

certainly be no excess of Silver. But it has been before shown that an excess of Nitrate of Silver in contact with the particles of Chloride of Silver, is essentially required for the perfection of the blackening process by Light; and therefore the rule is, always to apply the Chloride of Sodium first, and *afterwards* the Nitrate of Silver.

Sensitive papers prepared in this way with Chloride of Silver exhibit no *visible* indications of the presence of that salt until they are brought out to the light. The Chloride, being devoid of colour, is not seen amongst the surrounding tissue of the paper.

Iodide of Silver sensitive papers however are usually of a lemon-yellow tint, the characteristic colour of the salt being discernible.

C. SIMPLE EXPERIMENTS ILLUSTRATING THE ACTION OF LIGHT UPON CHLORIDE OF SILVER.

The various formulæ which are found convenient for the preparation of the solutions, etc., required in the practice of the Photographic Art, are given, as a general rule, in the second division of this work. In order however to save the reader any trouble which he might find in referring to that part at the present time, the following simple directions for the preparation of sensitive paper are appended.

Take of Chloride of Sodium, or Common Salt, 125 grains; distilled or rain water, 5 fluid ounces. Dissolve to form solution No. I.

Take of Nitrate of Silver 200 grains; distilled or rain water, 4 fluid ounces. Dissolve for solution No. II.

Cut a few squares of paper of the kind manufactured expressly for Photographic purposes, of about four inches in the side.

Pour the two solutions into separate plates to the depth of half an inch.

Place each square of paper upon the surface of solution

No. I. for three minutes, taking care that one side only is wetted; at the expiration of that time, remove and blot off with bibulous paper.

Then lay it upon the surface of solution No. II. in like manner, but for a longer time, viz. for five minutes; afterwards remove, and blot off as before.

Sensitive papers prepared in this way can be preserved for two or three days between the leaves of a book, and they will be found useful as we proceed in illustrating the various remarks which are made.

At present the following simple experiments may be performed with them, the idea being to convey a general notion of the susceptibility of the Chloride of Silver to receive the luminous impression.

Experiment No. I.—Place a square of the sensitive paper in the direct rays of the sun, and observe the gradual process of darkening which takes place; the surface passes through a variety of changes in colour until it becomes of a deep chocolate-brown. If the Light is tolerably intense, the brown shades are probably reached in from three to five minutes; however, the sensibility of the paper, and also the nature of the tints, vary much with the character of the organic matter present.

Experiment No. II.—Lay "a cross" or any other device cut from black paper upon a sheet of the sensitive paper, and compress the two together by means of a sheet of glass. After a proper length of exposure the figure will be exactly copied, the tint however being reversed; the black cross protecting the sensitive Chloride beneath, of course produces a similar one *white* upon a dark ground.

Experiment No. III.—Repeat the last experiment, substituting a piece of lace or gauze-wire for the paper device. This is intended to show the minuteness with which objects can be copied, since the smallest filament will be distinctly represented.

Experiment No. IV.—Take an engraving of any kind in which the contrast of light and shade is tolerably well marked, and having rendered it transparent by means of a heated Italian-iron rubbed with white wax, place it in contact with the sensitive paper, and expose as before. This experiment is meant to show that not only is the Chloride of Silver darkened by light, but that it is susceptible of darkening *in different degrees proportionate to the intensity of the light*, so that the *half* shadows of the engraving are accurately maintained, and a pleasing gradation of tone thereby produced.

D. ON THE SUPERFICIAL CHARACTER OF THE DECOMPOSITION OF THE SENSITIVE SURFACE BY LIGHT.

The amateur Photographer, whom we suppose to have been previously unacquainted with the nature of the changes produced upon the Chloride and Iodide of Silver by Light, will probably, at this stage of our inquiry, have conceived an erroneous notion *as to the extent of material* involved in those changes.

This error, if allowed to remain, may operate injuriously in a practical point of view, and therefore it will be desirable perhaps at once to dispel it.

Sensitive papers, prepared with the Chloride of Silver in the manner above directed, will naturally contain a considerable quantity of this salt, distributed not only upon the surface but also in the substance of the paper. It must not however be imagined that *the whole* of this Chloride, or indeed anything approaching thereto, is affected by the luminous radiations. The darkening which takes place is *exceedingly superficial*, and although the black colour may be intense, yet the amount of reduced Silver which goes to form it is so small that it cannot conveniently be estimated by chemical reagents.

Now a knowledge of the almost infinitesimal nature of

the changes which take place in Photography is practically useful, because it leads us to pay more attention to the condition of the *surface* of the sensitive salt, in contradistinction to the layer which lies immediately beneath.

It is particularly important to bear such a fact in mind in the preparation of the more sensitive papers containing the *Iodide of Silver*, and intended to be used in conjunction with a "developer" (*vide* next chapter), but it is also useful in the case of the ordinary Chloride of Silver paper just described.

For instance, if in preparing such paper the sheet be allowed to remain upon the salt solution until it is thoroughly saturated in every part, and then it be hung up by means of a pin to dry, the superficial stratum of liquid does not sink into the substance of the paper, but evaporates and leaves behind a layer of saline particles, which are certainly not favourably situated for subsequent photographic action.

On the other hand, if the sheet be removed at a somewhat earlier period, this same stratum of liquid is absorbed more or less completely, and the formation of *a crust* is avoided.

The kind of surface which it is desirable to obtain is just such an one as would be left after "blotting off" between sheets of bibulous paper, that is to say, a surface neither wet nor dry, but in an intermediate state; moist at first, and afterwards, when the evaporation is complete, leaving the particles in a fine state of division, and each one in contact with organic matter.

CHAPTER IV.

ON THE DEVELOPMENT OF AN INVISIBLE IMAGE BY MEANS OF A REDUCING AGENT.

It was shown in the last chapter that a prepared surface, either of Chloride, Bromide, or Iodide of Silver, in contact with excess of Nitrate of Silver, was susceptible of a peculiar change under the influence of Light, in virtue of which it became altered in colour and also in composition and properties.

Allusion is now to be made to another effect, produced upon these salts also by the agency of light, but differing from the former inasmuch as no *visible* change is brought about in consequence of it. The surface is in appearance precisely the same as before, but nevertheless it has undergone a modification of properties, which is shown by the fact that it becomes *blackened* when placed in contact with certain chemical reagents previously incapable of affecting it.

If sensitive paper, prepared with the *Iodide* of Silver in place of Chloride,* be exposed to the luminous rays for a period of time *insufficient to produce any visible de-*

* The Chloride of Silver is not so well adapted for employment in conjunction with a reducing agent as the Iodide of Silver. Although *theoretically* the nature of the change which takes place is the same in both instances, yet the Iodide possesses advantages over the other salt which cause it in practice to be universally adopted.

composition, and then—being transferred to a room from which the light of day has been carefully excluded—be brushed over with a solution of a substance known amongst chemists as *Gallic Acid*, it will be seen in a very short time to darken and change in colour until it becomes nearly black. On the other hand, papers which have not been exposed to the light, are unaffected by the Gallic Acid, so that it is evident that the action of the light is concerned in the production of the phenomenon.

In order to demonstrate this still more clearly, let a number of prepared sheets be shielded in certain parts by any opaque substance, and then, after the requisite exposure, treated with the Gallic Acid as before; in this case the protected parts remain white, whilst the others darken to a greater or less extent.

In the same way, copies of various objects, such as lace, leaves, etc., may be made, very much resembling those which result from the prolonged action of light alone. Hence we see that the object gained by the employment of the Gallic Acid is principally a *saving of time;*—the same effect as before is produced by a shorter exposure to light. A good idea of the surprising difference in the length of exposure required when *a developer* is used, may be obtained by a reference to some experiments conducted by M. Claudet. It was shown by him that in the case of a sensitive layer of the Bromo-Iodide of Silver the image was produced by an intensity of light *three thousand times less*, when the invisible image was developed by mercurial vapour, than if the light were allowed to act alone. Although with the pure Iodide of Silver the difference is probably less than this, it is still sufficiently remarkable.

To economize time by increasing the sensitiveness of the preparations, is a point of the utmost consequence with Photographers. Indeed, so far as *the use of the Camera* is concerned—from the low intensity of the luminous image

formed in that instrument—no other plan than the one above described would be practicable. Hence the advancement, and indeed the very origin, of the Photographic Art may be dated from the first discovery of a process for bringing out to view an invisible image by means of a developer.

The division of this chapter will be into three Sections: the first is the general nature of the reduction of metallic oxides; the second, the chemical properties of the substances usually employed as reducing agents; the third, a more minute account of the process of reduction applied to the Salts of Silver.

SECTION I.

The General Nature of Reduction of Metallic Oxides.

"Development" is essentially a process of *reduction*. Light alone reduces various Salts of Silver more or less completely to the metallic state. A developer does the same, but with greater rapidity and perfection; hence the composition of the deposit is more uniform than before, consisting probably in all cases of pure metallic Silver.

Reduction is opposed to *oxidation*. If we take a certain metal, we can by means of Nitric Acid impart oxygen to it, so that it becomes first an oxide, and afterwards, by solution of that oxide in the excess of acid, "a salt." After this salt is formed, by a series of chemical operations, the reverse of the former, it may be deprived of all its oxygen, and the metallic element again isolated as before.

Now the degree of facility with which "oxidation" as well as "reduction" is performed, depends much upon the affinity which the particular metal under treatment has for oxygen.

There is considerable difference in this respect. Some

metals combine with oxygen most eagerly, and are in consequence reduced with proportionate difficulty, whilst with others the reverse is the case.

As an illustration, take the two well-known metals, Iron and Gold; how speedily does the first become tarnished and covered with rust, whilst the other remains bright even in the fire! However, it is possible by a careful process to form "oxide of Gold;" but it retains its oxygen so loosely that a slight application of heat is sufficient to drive it off, and leave again metallic Gold.

Properties of the Noble Metals.—The various metallic elements are usually arranged in distinct classes according to the affinity they possess for oxygen, and to those having the least affinity the name of "noble metals" is given. They have acquired this honourable title from the capability they possess of preserving a bright metallic surface under the most unfavourable conditions. This property gives them a value superior to other metals which are more prone to rust and oxidation.

Silver, Gold, and Platinum are all noble metals, and their oxides are in consequence *unstable*. Any body which tends to absorb oxygen when brought into contact with these oxides, reduces them at once to the metallic state.

The substances employed by the Photographer, then, to assist the reducing action of the light, and so to develope the picture, *are bodies which tend to absorb oxygen. They reduce* the sensitive Salt of Silver to the condition of *metal* in the parts touched by light, and in that way they produce an opaque deposit which forms the image.*

* These remarks do not apply to the vapour of Mercury employed as a developing agent in the Daguerreotype. The chemistry of that process will be treated of in a separate chapter.

SECTION II.

Chemistry of the various Substances employed as Developers.

The most important of these bodies employed by the Photographer to develope the latent image are as follows:—Gallic Acid, Pyrogallic Acid, and the *Proto*salts of Iron.

CHEMISTRY OF THE GALLIC AND PYROGALLIC ACIDS.

a. *Of the Gallic Acid.*—Gallic Acid is obtained from "Gall Nuts," which are peculiar excrescences formed upon the branches and shoots of the *Quercus infectoria* by the puncture of a certain species of insect. The best kind is imported from Turkey, and sold in commerce as "Aleppo Galls." Gall Nuts do not contain Gallic Acid ready formed, but an analogous chemical principle termed "Tannic Acid," well known for its astringent properties and employment in the process of tanning raw hides.

Gallic Acid is produced by the *decomposition and oxidation* of Tannic Acid when the powdered galls are exposed for a long time in a moist state to the action of the air. Being only sparingly soluble in cold water, the acid is easily purified by crystallization. Gallic Acid is a very feebly acid substance; it is usually sold in the form of long silky needles of an astringent taste, which dissolve readily in boiling water, but are only sparingly soluble in the cold.

b. *Pyrogallic Acid.*—The term "pyro" prefixed to the Gallic Acid signifies that the new substance is obtained by the *action of heat* upon that body. At a temperature of about 410° Fahr., Gallic Acid is decomposed, and a white sublimate forms, which condenses in lamellar crystals; this is Pyrogallic Acid. Pyrogallic Acid is far more soluble in

cold water than the Gallic, and absorbs Oxygen with greater avidity, consequently it forms a more powerful developer. Although it is termed *an acid*, it may for all practical purposes be looked upon as a *neutral substance*, since it neither reddens litmus-paper nor forms salts with the alkaline bases.

The nature of the compound formed by the union of Gallic and Pyrogallic Acids with oxygen has not been determined.

CHEMISTRY OF THE PROTOSALTS OF IRON.

The combinations of Iron with Oxygen are somewhat numerous. There are two distinct oxides each of which forms a class of Salts, viz. the Protoxide of Iron, containing an atom of oxygen to one of metal; and the Peroxide, with an atom and a half of oxygen to one of metal. As *half atoms* however are not spoken of in chemical language, it is usual to say that the Peroxide of Iron contains three equivalents of oxygen to two of metallic Iron.

Expressed in symbols, the composition of the two is as follows:—

Protoxide of Iron, Fe O.
Peroxide of Iron, Fe_2O_3.

Now both of these oxides, as before said, form a class of salts with the various acids; but these salts do not at all resemble each other in their physical and chemical properties. The Protosalts are, usually speaking, of an apple-green colour, and form a solution in water which is almost colourless if not very highly concentrated. The Persalts, on the other hand, are dark, and give a yellow or even blood-red solution.

(A) Photographers we have to deal only with the Protosalts of Iron, but it is quite essential that we should understand the properties of both; therefore, in order to illustrate what has been said, let the student take a crystal of

Protosulphate of Iron, or Green Vitriol as it is termed in commerce, and, having reduced it to a powder, pour a little Nitric Acid upon it in a test-tube. On the application of heat, abundance of fumes will be immediately given off, and a red solution will be obtained. The liquid contains no longer a *Proto*sulphate but a *Per*sulphate of Iron: the Nitric Acid, as usual, has acted as an oxidizing agent.

Here then we have another distinctive peculiarity of the Protosalts of Iron—they tend to absorb oxygen and pass into the condition of Persalts. This tendency it is which gives them their value as reducing agents.

There are two different Protosalts of Iron commonly employed by Photographers: these are the Protosulphate and the Protonitrate of Iron.

a. *Protosulphate of Iron.*—This is the Copperas or Green Vitriol of commerce, a most abundant substance, and used for a variety of purposes in the arts. Commercial Sulphate of Iron however, being prepared on a large scale, mostly requires recrystallizing in order to render it sufficiently pure for Photographic purposes.

Pure Sulphate of Iron is met with in the form of large transparent, prismatic crystals, of a delicate green colour; by exposure to the air they gradually absorb Oxygen and become rusty on the surface. Solution of Sulphate of Iron, colourless at first, afterwards changes to a red tint, and deposits a brown powder; this powder is a *basic* Persulphate of Iron, that is to say, a Persulphate containing an excess of the oxide, or "base." By adding Sulphuric Acid to the solution of Protosulphate of Iron, the formation of *a deposit* is prevented, but the decomposition goes on slowly as before.

b. *Protonitrate of Iron.*—This salt does not occur in commerce, but is prepared by double decomposition between Nitrate of Lead and Protosulphate of Iron. (See Part II. of this work.)

Protonitrate of Iron is too unstable to be crystallized without great difficulty; its aqueous solution is pale green at first, but very prone to decomposition, even more so than the corresponding Sulphate.

SECTION III.

The Reduction of the Salts of Silver.

Having given a general sketch of the reduction of metallic oxides, and of the main properties of the principal substances employed to develope the latent image, we are in a condition to enter more minutely into the exact nature of the process.

First, the reduction of the *Oxide* of Silver will be described, as the most simple illustration; then that of *Salts* of Silver containing Oxygen-acids; and lastly, the Salts of Silver with *Chlorine, Iodine*, or *Bromine*.

A. REDUCTION OF OXIDE OF SILVER.

In order to illustrate this properly, it is necessary that the Oxide of Silver should be in a state of solution. Now Oxide of Silver does not dissolve to any great extent in water, but it is abundantly soluble in *Ammonia*, and the liquid known amongst chemists as the "Ammonio-Nitrate of Silver" is a solution of that kind.

Therefore, if a little of this Ammonio-Nitrate of Silver be placed in a test-tube, and Pyrogallic Acid be added to it, very shortly the whole becomes discoloured, and a deposit settles to the bottom.

This deposit is metallic Silver, and it is formed by the removal of the oxygen previously combined with Silver in the form of *Oxide*. Although the Oxide of Silver is soluble in Ammonia, *metallic Silver* is not, and therefore it immediately subsides in the form of a *precipitate*.

B. REDUCTION OF THE OXYACID SALTS OF SILVER.

By the term Oxyacid Salts, is signified those salts which contain the oxide of Silver intimately combined with oxygen-acids; as *e. g.* the *Nitrate* of Silver, the *Sulphate*, the *Acetate* of Silver, etc.

Now all such salts are reduced by developers in the same manner as the Oxide of Silver alone; but what we notice now is, that they are reduced *with proportionate difficulty.*

The developer having no affinity *for the acid*, but only for the Oxygen contained in the base of the salt, the presence of this acid is always a hindrance, and the process of reduction proceeds more slowly than before.

The degree to which the retarding effect is noticed, depends upon *the strength of the acid* contained in the salt. Nitric Acid is a very powerful body. Acetic Acid is feeble; hence the *Nitrate* of Silver requires a more active reducing agent to cause a deposit of metal from it in a certain time, than the *Acetate* of Silver does.

C. REDUCTION OF THE HYDRACID SALTS OF SILVER.

By the term "Hydracid" is meant those Salts of Silver which do not contain oxygen, or oxygen-acids, but simply elements like Chlorine or Iodine combined with Silver. These same elements are characterized by forming *acids* with *Hydrogen*, which acids are hence called "*Hydr*acids." Hydrochloric Acid (HCl) is an example; so also is Hydriodic Acid (HI). Now the reduction of the Hydracid Salts requires to be discussed separately from the last, because it will no doubt occur at once to the mind of the reader that the mode of action must in their case be somewhat different from that already described.

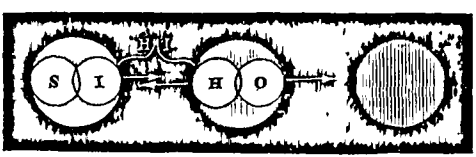
The reducing agent tends to absorb *Oxygen*, but here is no oxygen to be absorbed! On the other hand, it has

no attraction for Chlorine or Iodine, by which elements the Oxygen is replaced in these Hydracid Salts.

The explanation of this apparent difficulty is as follows: When a Chloride or Iodide of a noble metal is reduced by a developer, *an atom of water* may be supposed to take a part in the reaction. This atom of water consists of *Oxygen* and *Hydrogen:* the former of which elements passes to the developer, the latter to the Chlorine or Iodine, as the case may be.

By a reference to Part III. it will be seen that the class of elementary substances to which Chlorine belongs are characterized by having a strong affinity for *Hydrogen* as well as for the metals; therefore the decomposition of a Chloride or Iodide of Silver in the reaction we have now explained is facilitated by the fact of this atom of Hydrogen being at hand, ready to combine with the Chlorine or Iodine immediately on their separation from the Silver.

Perhaps the following simple diagram may assist the comprehension of the change.



Compound Atom of Iodide of Silver. Compound Atom of Water. Atom of Gallic Acid.

The letter S stands for Silver, I for Iodine, H for Hydrogen, and O for Oxygen.

Observe that the molecules H and O separate from each other and pass in opposite directions; O unites with the Gallic Acid; H meets I, and forms with it an atom of Hydriodic Acid; whilst S, the atom of Silver, is left alone.

On the Presence of a soluble Salt of Silver as favouring the Reduction of Chloride and Iodide of Silver.—There is

no reason whatever, upon theoretical grounds, why the Iodide of Silver *plus* an atom of water should not suffer reduction upon the application of a developer. The *Chloride of Gold*, which is a corresponding salt of a noble metal allied to Silver, very quickly deposits metallic Gold when mixed with Gallic Acid, and the supernatant liquid is found to contain free Hydrochloric Acid (HCl).

Nevertheless a sensitive layer of Iodide of Silver *does not blacken* by Gallic Acid even in the open light of day. The only way of accounting for the fact is, to suppose that the *insolubility* of the Iodide is an impediment to its reduction. The Chloride of Gold in the above experiment, being *in a state of solution*, is brought more perfectly into contact with the reducing agent, whereas in the case of the Iodide of Silver the Gallic Acid is unable to reach the particles, and therefore the process cannot be established.

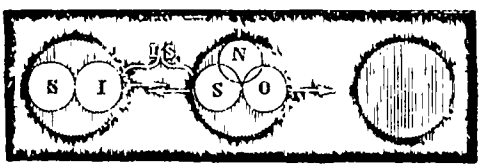
Now if the same layer of Iodide of Silver, which when in a pure state was found to resist the action of the developer, be dipped for a moment in a solution of Nitrate, or Acetate, or, in fact, in any *soluble* Salt of Silver, and then in the open daylight be again treated with Gallic Acid, immediately it blackens intensely. Therefore either one of two things must have happened: the soluble Silver Salt has in some way been the means of facilitating the reduction of the Iodide, or it has been itself reduced, the Iodide remaining as before.

Both of these views have their respective supporters, and will be again alluded to in the 7th Chapter, when we speak of the action of Light upon the sensitive film. At present we treat only of the former hypothesis, viz. that the presence of soluble Nitrate of Silver facilitates the reduction of Iodide of Silver.

It may be supposed to do so exactly in the same way as that before attributed to "the atom of water," viz. by furnishing an elementary basis with which the separated Io-

dine may recombine. The atom of water offers a molecule of *Hydrogen;* the Nitrate, a molecule of *Silver*. Now Iodine has an attraction for Hydrogen, but it has a greater attraction still for Silver, consequently the Nitrate prevails and determines the reduction by the developer; whereas, from the impediment caused by the insolubility of the Iodide, the atom of water failed to do so.

The following diagram, closely corresponding to the last, will illustrate what is meant.



Compound Atom of Iodide of Silver. Compound Atom of Nitrate of Silver. Atom of Gallic Acid.

S stands for Silver as before, and N for Nitric Acid. Observe that the compound atom of Nitrate of Silver contains a molecule of Oxygen for the developer, a molecule of Silver for the separated Iodine, and an atom of Nitric Acid, which is liberated, and takes no further part in the change.

From a consideration of this diagram it will also be seen how impossible it must be for the chemist to decide, without further investigation, as to which of the two compound atoms furnishes the Silver of the image; since, even supposing the Iodide of Silver to be decomposed, the separated Iodine immediately re-forms it by combining again with Silver derived from the Nitrate.

D. ON THE ACTION OF LIGHT AS DETERMINING THE REDUCTION OF SALTS OF SILVER BY A DEVELOPER.

The reader is already aware that the agency of light alone, without any developer, reduces the salts of Silver by degrees to the metallic state, and that this is especially

the case when *Organic matter* and *free Nitrate of Silver* are present, in conjunction with the Chloride or Iodide. Such reduction however can only take place by a comparatively *prolonged* exposure, and therefore it is at once contradistinguished from another effect to which allusion also has been made, and which may be termed *the instantaneous agency of light*, in accelerating the process of reduction.

The sensitive surface of Iodide of Silver, even when in contact with a due proportion of Nitrate of Silver, is not readily affected by the developer in the dark. A preliminary exposure to light however, even although it be comparatively momentary, entirely alters the whole state of things, and the reduction then proceeds with rapidity.

Plainly the nature of the action of light is such as to produce a disturbance of some kind upon the surface of the Iodide of Silver, which causes that Salt to behave towards the reducing agent in a manner different from what it otherwise would have done.

At the present time we content ourselves with distinguishing carefully between this effect of "light" as favouring reduction by a developer, and the direct action of light alone. In a future chapter the subject will be entered into more deeply, and hypotheses will be brought forward tending as far as possible to assist the comprehension of the phenomena.

E. ON THE VARIED APPEARANCES PRESENTED BY METALLIC SUBSTANCES WHEN IN A STATE OF FINE DIVISION.

In conducting various experiments intended to illustrate the reduction of metallic Silver from solutions of the Oxide and of its Salts, the amateur will probably be often surprised at the tint assumed by the deposit.

Sometimes it appears to be *black;* occasionally *yellowish;* often *white and sparkling.*

These differences in colour do not depend, as might be

supposed, upon *differences in composition*, but simply upon a slight variation in the molecular arrangement of the particles. Other metals exhibit the same peculiarity. Platinum and Iron, which are both susceptible of a high polish and lustre, are dull and intensely black when in the state of fine powder. Gold is purplish-brown. Mercury a dirty grey. The varieties observed in the appearance of the reduced Silver depend much upon the nature of the agent selected for the precipitation. Gallic and Pyrogallic Acid often give a dense black powder. The Salts of Iron, on the other hand, especially when Nitric Acid is added, produce a sparkling deposit resembling what is termed frosted Silver.

The manner in which the deposit is viewed also modifies its appearance: if laid in contact with a sheet of white paper, it appears dark by contrast, but when backed up with black velvet assumes a lighter tone.

These remarks are sufficient for our present purpose. They are given with the idea of preventing a slight degree of confusion which might perhaps otherwise arise.

RECAPITULATION OF MAIN FACTS STATED IN THIS CHAPTER.

The development of a latent image is produced by a reduction of metallic Silver taking place at those parts of the plate which appear to be blackened.

The developing agent causes the reduction by absorbing Oxygen previously in combination with Silver. The Protosalts of Iron are thus converted into red Persalts, and the Gallic and Pyrogallic Acids form more highly oxidized compounds, the nature of which has not been determined.

There is no *theoretical* difficulty in an *Iodide* of Silver being reduced if we associate with it an atom of Water to furnish the Oxygen for the developer, but practically speaking we are unable to get evidences of reduction unless some *soluble salt* of Silver is also present. This

soluble salt probably acts in the same way as the atom of water would do, but with more energy: it supplies the developer with Oxygen, and the separated Iodine with another atom of Silver in place of the one it had lost.

Lastly, that *the action of Light* plays a very important part in the reduction, by a developer, of Iodide of Silver *plus* soluble Nitrate of Silver; that it affects the Iodide in a peculiar way, so as to produce a marvellous acceleration of the blackening process; and that for this a comparatively instantaneous exposure only is required.

CHAPTER V.

ON "FIXING" THE PHOTOGRAPHIC IMAGE.

It is easily seen, from a very slight consideration of the circumstances of the case, that a sensitive layer of Chloride or Iodide of Silver, on which an image has been formed either with or without the aid of a developing agent, must require to pass through some further treatment in order to render it indestructible by diffused light.

It is true that the *image itself* is sufficiently permanent, and therefore cannot be said, in correct language, to need any *fixing;* but *the unchanged Silver Salt* which surrounds it, being still sensitive to light, tends of course to be decomposed in its turn, and in that way to obliterate the effect.

Therefore we may, if we wish it, speak of "disengaging" the image, instead of fixing it; but whichever term be employed, the important point to be remembered is—that it is necessary to remove the unaltered Chloride or Iodide of Silver which surrounds the image, in order to render the proof permanent and unalterable either by *time* or *light.*

The removal of these Salts is effected by the use of some chemical agent which possesses the property of *dissolving* them. The list of solvents of Chloride and Iodide of Silver has already been given in Chapter II., but it does not

follow that a selection of either of these may be made indifferently. In order that any body may be employed with success as a "fixing" agent, it is necessary not only that it should dissolve unchanged Chloride or Iodide of Silver, *but also that it should produce no injurious effect upon the same salts reduced by light.*

This *solvent action upon the image*, as well as upon the parts which surround it, is most liable to happen when the agency of light alone, without any developer, has been employed. In that case the composition of the darkened parts is less different from the others; *they are reduced somewhat, but they are not reduced perfectly to the metallic state;* hence a portion of their old solubility remains.

The student will invariably find, that in fixing the proofs upon Chloride of Silver paper, he is obliged to be more cautious than usual, and to abstain from the employment of the most energetic solvents, lest a portion of the darkened Chloride should be dissolved away.

CHEMISTRY OF THE VARIOUS FIXING AGENTS, WITH THEIR RESPECTIVE PECULIARITIES OF OPERATION.

The following will be mentioned:—Ammonia—Alkaline Chlorides—Alkaline Iodides—Alkaline Hyposulphites—Alkaline Cyanides.

A. AMMONIA.

For a sketch of the chemistry of this liquid the student is referred to Part III. Ammonia dissolves *Chloride of Silver* readily, but it does not dissolve *Iodide of Silver:* hence, if employed at all, its use must necessarily be confined to the paper proofs upon Chloride of Silver. It is not found however to be well adapted even for these, the solvent action being too energetic, and the dark tones in consequence being injured.

B. ALKALINE CHLORIDES.

The Chlorides of Potassium, Ammonium, and Sodium (see Part III.) all dissolve a small portion of Chloride of Silver if they are used in a concentrated state.

The earlier Photographers employed a saturated solution of common Salt, Chloride of Sodium, for fixing paper prints; but they did so simply because they were unacquainted with other substances which would succeed better. The fixing action of the Alkaline Chlorides is always slow and imperfect, and their use may now be said to be obsolete.

C. ALKALINE IODIDES AND BROMIDES.

The Iodide and Bromide of Potassium have both been employed as fixing agents; but they are too expensive for general use, and especially as the same result can be obtained by means of other salts which are cheaper and more readily procured.

Peculiarities of the Alkaline Iodides used as Fixing Agents.—There are some points worthy of comment in the solution of Iodide of Silver by these salts, viz. that the amount dissolved is not in proportion to the *quantity* of the Iodide or Bromide of Potassium, but rather to *the degree of concentration of their aqueous solutions.*

This is not by any means common with solvents which act by entering into chemical combination with the substance dissolved. Usually speaking, in such a case, a given weight of the one salt dissolves a given weight of the other, independently of the amount of water which is present. The peculiarity in the action of Iodide of Potassium depends upon the fact that the double salt formed, viz. the Iodide of Potassium and Silver, is not soluble in, but rather *decomposed by*, a large quantity of water.

This is well seen in the preparation of the ordinary Calotype sensitive paper. The sheet is first soaked in a strong

solution of the double Iodide compound, and then transferred to a vessel of water. The effect of this is to dissolve out the alkaline Iodide completely, and to leave the Iodide of Silver in the fibres of the paper. It is necessary then, in using the alkaline Iodides or Bromides as fixing agents, to bear in mind that *strong solutions* of the salts are alone adapted for the purpose; the same remark also applying to the Chloride of Silver dissolved in Chloride of Sodium.

D. ALKALINE HYPOSULPHITES.

The discovery of the peculiar properties possessed by the Hyposulphites forms quite an era in the history of Photography.

At present we speak of them only as "fixing agents," but in a future chapter it will be shown that they are useful also in imparting agreeable tones to the paper Photographs upon Chloride of Silver.

Chemistry of the Hyposulphites.—Hyposulphurous Acid is one of the Oxides of Sulphur. It is, as its name implies, of an acid nature, and takes its place upon the list immediately below the "Sulphurous" Acid ("*upo*," under).

The Hyposulphite of Soda, as commonly found in commerce, is a neutral combination of Hyposulphurous Acid with the alkali Soda. Hyposulphite of *Potash* or of *Ammonia* would succeed equally well with the Hyposulphite of Soda, but the latter is chosen as being the most economical salt in the preparation.

Hyposulphite of Soda occurs in the form of large translucent groups of crystals; these crystals are soluble in water almost to any extent, and their solution is attended with the production of cold; they have a nauseous and bitter taste.

Chloride and Iodide of Silver both dissolve in solution of Hyposulphite of Soda, but not to the same extent. The

former salt is the more soluble of the two. The nature of the resulting solution is not what it would at first seem to an inexperienced chemist. We cannot speak of it *correctly* as Chloride of Silver dissolved in Hyposulphite of Soda, since a chemical decomposition takes place during the process of solution.

The action of Hyposulphite of Soda upon Chloride of Silver is thus represented (of course that with the *Iodide* is similar):—

Hyposulphite of Soda in excess *plus* Chloride of Silver
equals Double Hyposulphite of Soda and Silver
and Chloride of Sodium.

or, in symbols:—

$$3\,NaO\,S_2O_2 + AgCl = 2NaNaO\,S_2O_2, AgO\,S_2O_2 + NaCl.$$

Observe—that the atom of Chlorine has taken to itself an atom of Sodium, and exists in combination with it as Chloride of Sodium, or common Salt. The Silver in the solution is not present in the state of Chloride, but as Hyposulphite of Silver, which forms a soluble double Salt with two atoms of Hyposulphite of Soda. This soluble double Salt can be crystallized out by carefully evaporating the solution. It is a substance possessing a most intensely *sweet* taste, which is sufficiently remarkable, seeing that both Hyposulphite of Soda and Nitrate of Silver are disgustingly nauseous and bitter.

Sir John Herschel has pointed out the existence of another double Hyposulphite of Soda and Silver, which differs in composition from the former, in containing only one atom of Hyposulphite of Soda instead of two. It is produced by the addition of Chloride or Nitrate of Silver to a solution of Hyposulphite of Soda already nearly saturated with Silver Salts. It is *insoluble* in water.

Peculiarities of Hyposulphites as Fixing Agents.—Hyposulphite of Soda is employed for fixing all kinds of

Photographic pictures, the solution of it kept for that purpose being technically termed "The Hypo Bath." For fixing paper proofs upon Chloride of Silver the Hypo Bath must not be allowed to become saturated, otherwise the Silver Salt will be converted into the *insoluble* double Hyposulphite instead of being dissolved.

It appears, according to the observations of Dr. E. W. Davy in the 'Photographic Journal,' vol. i. p. 158, that the difference between the solubility of the Iodide and Chloride of Silver in Hyposulphite of Soda is accounted for in this way:—during the solution of the former Salt, *Iodide of Sodium* is formed, and this alkaline Iodide exercises a prejudicial effect upon the continuance of the process.

Alkaline *Chlorides* have not the same action; neither have alkaline *Bromides;* consequently the Silver compounds corresponding to them dissolve with greater facility.

E. ALKALINE CYANIDES.

The Chemistry of Cyanogen and Cyanides is described in Part III.

No doubt the reader is familiar with the properties of the fluid sold under the name of *Prussic Acid.* Now Prussic Acid is a Cyanide of *Hydrogen,* and the fixing agent used by Photographers is a Cyanide of *Potassium;* consequently, as might have been expected, the two substances are in their nature very similar. It is most important to bear this in mind, as suggesting the necessity of extreme caution in the employment of the Cyanide of Potassium, on account of the highly poisonous qualities it possesses.

Properties of the Cyanide of Potassium.—Cyanide of Potassium is not often met with in commerce in the form of crystals, but rather in lumps of considerable size, which have evidently undergone fusion. In this state it is com-

monly associated with a large percentage of the *Carbonate of Potash;* and this is the reason why operators are not more nearly agreed as to the quantity of the salt which should be taken for dissolving.

Cyanide of Potassium is a deliquescent salt, and very soluble in water; the solution is always more or less subject to decomposition, and in a very short time begins to evolve the odour of Prussic Acid.

Peculiarities of the Cyanide as a Fixing Agent.—The Cyanide is a most energetic agent for dissolving the insoluble Silver Salts; far more so, in proportion to the quantity used, than even the Hyposulphite of Soda. The Salts are in all cases converted into Cyanides, and exist in the solution in the form of soluble double Salts. Cyanide of Potassium is not adapted for fixing positive proofs upon Chloride of Silver; and even when a developer has been used, unless the solution of Cyanide is tolerably dilute, it is apt to attack the image and dissolve away portions of it more or less.

CHAPTER VI.

ON THE NATURE AND PROPERTIES OF LIGHT.

THE student would find it to be a constant source of embarrassment to him in the prosecution of his experiments, if he were to neglect to acquaint himself beforehand with some of the more remarkable properties of Light. It is therefore intended to devote the following chapter to a discussion of that subject, the object being to select the most prominent points, and to state them as clearly as possible, referring, for information of a more complete kind, to acknowledged works on the subject of Optics.

The chapter will be divided into three Sections:—first, the compound nature of Light and the means whereby it may be demonstrated; second, the laws of refraction of Light; and third, the construction of Lenses and of the Photographic Camera.

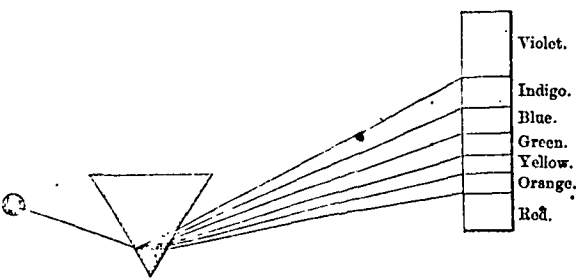
SECTION I.

The Compound Nature of Light.

This Section includes the following subdivisions:—A. The decomposition of white light into elementary coloured rays.—B. Division of the elementary rays into luminous, heat-producing, and chemical rays.—C. The practical importance of such a division.

A. THE DECOMPOSITION OF WHITE LIGHT INTO ELEMENTARY COLOURED RAYS.

The ideas which were entertained on the subject of Light, previously to the time of Sir Isaac Newton, were of the most vague and unsatisfactory nature. It was shown however by that eminent philosopher, that a ray of sunlight was not, as had been supposed, of a *homogeneous nature*, but in reality consisted of several rays of different vivid colours, united together and intermingled. This can be demonstrated by throwing a pencil of Sunlight upon one angle of a "prism," and receiving the oblong image, so formed, upon a white screen.



The space illuminated and coloured by a pencil of rays analysed in this way is called "the Solar Spectrum." Without inquiring at present into the cause of the decomposition, which will be explained as we proceed, we notice that seven principal colours may be distinguished in the Solar Spectrum, viz. red, orange, yellow, green, blue, indigo, and violet. It was imagined by Sir Isaac Newton that these were in reality the *primary* colours of white Light; but Sir David Brewster has shown more recently that such is not the case,—that the primary colours are only *three* in number, viz. red, yellow, and blue, and that the others

are produced by two or more of these overlapping each other: thus the red and yellow spaces intermingled constitute *orange;* the yellow and blue spaces, *green;* and so with the rest.

The composition of white light from the seven prismatic colours may be roughly proved by painting them upon the face of a wheel, and causing it to rotate rapidly; they then appear as if blended together, and a sort of greyish-white is the result. The white is imperfect, because the colours employed cannot possibly be obtained of the proper tints or laid on in the exact proportions.

Other Means of decomposing White Light.—The decomposition of light may be effected in many ways besides by passing it through a prism.

First, by *reflection* from the surfaces of "coloured" bodies. All substances throw off rays of light in greater or less quantity from their surfaces, which rays impinge upon the retina of the eye and produce the phenomena of vision. *Colour* is caused by *portion only*, and not the whole of the elementary rays, being projected in this way. Surfaces which are termed "white" reflect all the rays alike; coloured surfaces absorb some and reflect others: thus "red" substances reflect only red rays, "yellow" substances, yellow rays, etc., the ray which is reflected in all cases deciding the colour of the substance. Why this should be, or to what peculiar molecular condition the difference is to be attributed, it is not possible to say.

Secondly, light may be decomposed by *transmission* through certain "media" which are transparent to some rays but opaque to others.

"White" glass allows all the rays constituting white light to pass. By the addition of certain metallic oxides, however, its properties are modified in such a way as to interfere with the passage of particular rays, whilst to others no impediment is offered. Hence the varieties of

"coloured glass"—the observed colour being in all cases the one which is transmitted.

B. DIVISION OF THE ELEMENTARY RAYS INTO LUMINOUS, HEAT-PRODUCING, AND CHEMICAL RAYS.

Independently of any hypothesis which may be entertained upon the nature of Light, it is clear that it produces a variety of distinct effects upon the bodies which surround us. These effects may be classed together as "the properties of light." They consist of three kinds—first, the phenomena of colour and vision; second, of heat; and third, of chemical action.

Without entering deeply into the subject, we observe at present that these various properties are not possessed by all the elementary rays in common, but that each one belongs exclusively to a particular ray in preference to the rest. Taking the three primary colours, blue, yellow, and red, we assign to each its respective peculiarity of action.

The *yellow* is decidedly the most luminous ray, and the phenomena of vision are due to it. On examining the Solar Spectrum, it is seen that the brightest part is that occupied by the yellow ray, and that the light diminishes rapidly on either side. So also apartments, etc. glazed with yellow glass, always appear abundantly illuminated, whilst the effect of red or blue glass is dark and sombre.

The *heating properties* of the sunlight reside principally in the red ray, as is shown by the expansion of a mercurial thermometer placed at that part of the Spectrum.

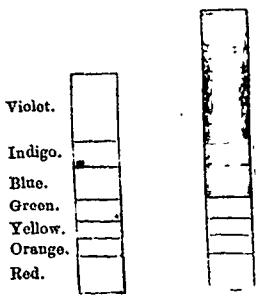
Lastly, the third distinctive property of light, viz. its *chemical action*, is associated with the *blue* ray in preference to either the red or the yellow.

As it is important to impress upon the mind the differences in chemical power possessed by coloured rays of

light, the following experiments may be performed for that purpose.*

Experiment No. I.—Expose a layer of Iodide of Silver to the prismatic Spectrum for a short time, and then proceed to bring out the effect produced, by means of a developing agent. It will be seen that the darkening is the most decided in the Indigo and Violet spaces, and that it extends upwards to a considerable distance, even beyond the visible spectrum. If traced in the opposite direction, it is found to diminish rapidly in intensity until it reaches the green-coloured space, and then to cease entirely.

The following diagrams are intended to illustrate this.



VISIBLE SPECTRUM. CHEMICAL SPECTRUM.

Experiment No. II.—Select a vase of flowers of different shades of scarlet, blue and yellow, and make a photographic copy of them upon Iodide of Silver. The blue tints will be found to act most violently upon the sensitive compound, whilst the reds and yellows are scarcely visible; probably they would not be seen upon the plate at all were it not that it is difficult to procure in nature

* Probably the last of these experiments (No. III.) is the only one which will be practicable for the student at this early stage of his inquiries; but he may return to the others with advantage after having completed the study of the chapters which follow.

pure and homogeneous tints which are free from admixture with other colours.

Experiment No. III. — This experiment is extremely simple, and perhaps more convincing than either of the others. Take a sheet of sensitive paper prepared with Chloride of Silver, and lay upon it strips of blue, yellow, and red glass. On exposure to the sun's rays for a few minutes, the part beneath the blue glass darkens rapidly, whilst that covered by the red and yellow glass is perfectly protected. This result is the more striking from the extreme *transparency* of the yellow glass, giving the idea that the Chloride would certainly be blackened first at that point. On the other hand, the blue glass appears very dark, and effectually conceals the tissue of the paper from view.

C. THE PRACTICAL IMPORTANCE OF DISTINGUISHING BETWEEN VISUAL AND CHEMICAL RAYS OF LIGHT.

The distinction between visual and chemical rays of light is important to the Photographer in many ways. Were the force producing "actinic," or chemical change, the same in all respects as that appertaining to vision, it would be difficult and indeed almost impossible to make any use whatever of the more sensitive chemical preparations. How could they be prepared beforehand, being so delicately sensible to the influence of light? All the details of manipulation must under such circumstances be conducted *absolutely in the dark!* It is true that Photographers now make use of a dark room for preparing the plates; but it is dark only in a chemical sense: in other words, it is illuminated by means of a homogeneous yellow light, which, at the same time that it enables the operator to see the progress of the work, produces no injurious effect upon the sensitive surfaces.

Another point connected with the same subject and

worthy of note is—the extent to which the sensibility of the Photographic compounds is influenced by atmospheric conditions not visibly interfering with the *brightness* of the light. It is natural at first to suppose that those days on which the sun's rays are the most powerful would be the best for rapid impression, but that is not by any means the case. If the light is at all of a yellow cast, however bright it may be, its "actinic" powers will be very small.

The artist will frequently have occasion to notice, whilst prolonging his labours until the evening, that a sudden diminution of the sensibility of the plates begins to take place at a time when perhaps but little difference can be detected in the brilliancy of the light. The setting sun has sunk behind a golden cloud, and all chemical action is soon at an end.

In the same manner is to be explained the difficulty of obtaining Photographs in the glowing light of tropical climates—the superiority in this respect of the early months of spring over those of the midsummer—of the morning sun to that of the afternoon, etc.

Also, by establishing a strict distinction between chemical and luminous influence, many terms now constantly in use are found to be inaccurate. The word "Photography," for instance, signifies the taking of pictures by means of *Light*, whereas it is in reality not *light* which produces the change. In every science similar examples of inaccurate nomenclature may be found; but it is never desirable to attempt to discard a term which has been familiarized to us by long use.

SECTION II.

The Refraction of Light.

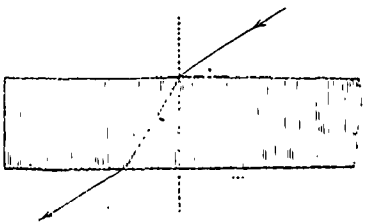
The subdivisions of this Section are five in number:—

A. The phenomena of simple refraction by parallel and in-

clined surfaces.—B. Refraction from curved surfaces.—C. Explanation of the decomposition of white light by prisms and lenses.—D. The foci of lenses.—E. The formation of a luminous image by a lens.

A. PHENOMENA OF SIMPLE REFRACTION BY PARALLEL AND INCLINED SURFACES.

A ray of light, in its passage through any transparent medium, always travels in a straight line as long as the density of the medium continues unchanged. But if the density varies, becoming either greater or less, then the ray is "refracted," or bent out of the course which it originally pursued. The degree to which the refraction or bending takes place depends much upon the nature of the new medium, and in particular upon its *density* as compared with that of the medium which the ray had previously traversed. Hence Water refracts light more powerfully than Air, and Glass more so than Water. The following diagram illustrates the refraction of a ray of light.



The dotted line is drawn perpendicularly to the surface, and it is seen that the ray of light on entering is bent *towards* this line. On emerging, on the other hand, it is bent to an equal extent *away from the perpendicular*, so that it proceeds in a course parallel to, but not coincident with, its original direction. If we suppose the new medium, in place of being more dense than the old, to be *less*

dense, then the conditions are exactly reversed,—the ray is bent away from the perpendicular on entering, and towards it on leaving.

It must be observed that the laws of refraction apply only to rays of light which fall upon the medium *at an angle;* if they enter perpendicularly—in the direction of the dotted lines in the last figure—they pass straight through without suffering any refraction.

Notice also, that it is *at the surfaces of bodies* that the deflecting power acts. The ray is bent on entering, and bent again on leaving; but whilst it is within the medium it continues in a straight line. Hence it is evident that by variously modifying the surfaces of refractive media the rays of light may be diverted almost at pleasure. This perhaps will be made more clear by a few simple diagrams.

Fig. 1.

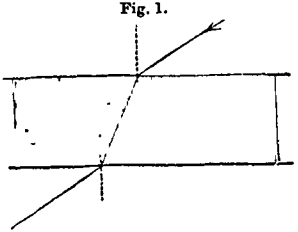


Fig. 2.

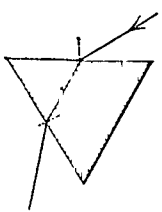


Fig. 3.

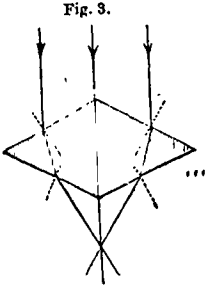


Fig. 4.

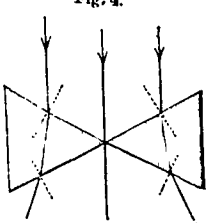


Fig. 2 is termed "a prism;" fig. 3 consists of two prisms placed with their bases in contact, and fig. 4, of two prisms placed edge to edge. In accordance with the usual law, a prism such as fig. 2 bends the ray permanently to one side; two prisms placed base to base cause rays before parallel to meet in a point; and conversely, prisms placed edge to edge divert them further asunder.

B. ON THE VARIOUS FORMS OF LENSES.

The phenomena of the refraction of light are seen in the case of *curved* surfaces, as well as with those which are plane.

Glasses ground of a curvilinear form are termed "Lenses." The following are examples.

Fig. 1. Fig. 2. Fig. 3.

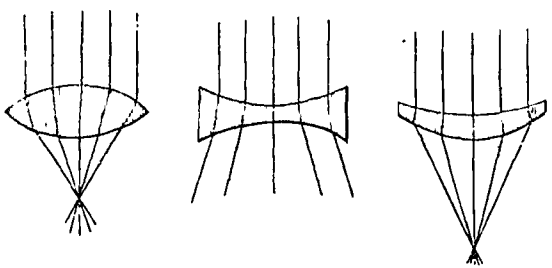


Fig. 1 is a "biconvex" lens; fig. 2, a "biconcave," and fig. 3, a "concavo-convex" or "meniscus" lens.

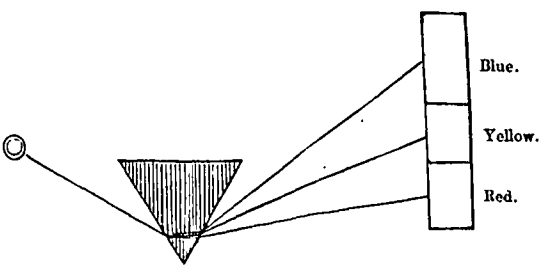
As far as their refractive powers are concerned, these figures may equally well be represented by others bound by straight lines, thus:—

It is seen at once, from observations already made, that

a biconvex lens must tend to condense rays of light to a point, and a biconcave to scatter them. A meniscus combines both actions, the ultimate effect depending upon the ratio which the radii of the two curves bear to each other.

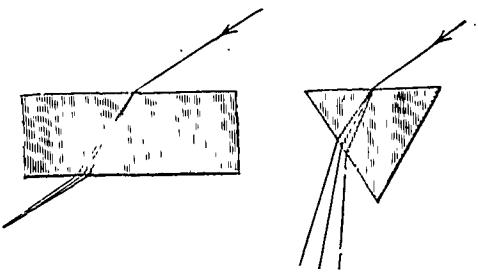
C. EXPLANATION OF THE DECOMPOSITION OF WHITE LIGHT BY PRISMS AND LENSES.

It was stated in the first section of this chapter that white Light might be decomposed into its elementary coloured rays by passing it through the outside edge of a prism. We are now in a condition to understand the *rationale* of this. All the coloured rays are refrangible, but they are not all *refrangible to the same extent.* Of the three primary colours the *Blue* is the most so, and the *Red* the least, consequently the blue occupies the highest space in the spectrum.



A little reflection will serve to show that if, as just stated, the coloured rays are unequally refrangible, white light must, as a consequence, be invariably decomposed on entering any dense medium. This is indeed the case; but if the surfaces of that medium *are parallel to each other*, the effect is not seen, because the rays again recombine on their emergence, being bent to the same extent in the opposite direction. When however the surfaces are not

parallel; but *inclined to each other at an angle*, the original divergence being increased, the decomposition becomes permanent. The following figures will show what is meant.



D. ON THE FOCI OF LENSES.

It has already been shown that convex lenses tend to condense rays of light and bring them together to a point. This point is termed "the focus" of the Lens.

The following laws as regards the focus may be laid down.

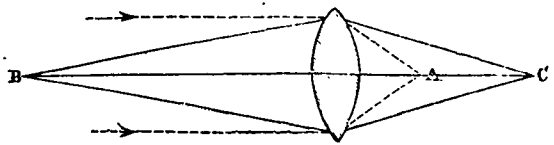
That rays of light which are pursuing a parallel course at the time they enter the Lens are brought to a focus at a point nearer to the Lens than others.

That divergent rays, on the other hand, do not meet so speedily,—their focus is longer.

Now "parallel rays" are rays proceeding from distant objects, and "diverging rays" are rays from objects near at hand. The Sun's rays are always "parallel," and the divergence of the others becomes greater as the distance from the Lens is less.

The focus of a Lens for parallel rays is always termed the "principal focus," and it is not subject to variation. When the rays are not parallel, but diverge from a point,

then that point is associated with the focus, and the two together are termed "conjugate foci."

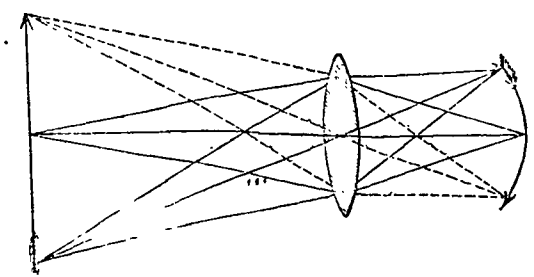


In the above diagram A is the principal focus, and B and C are conjugate foci. Any object placed at B has its focus at C, and conversely when placed at C it is in focus at B.

Therefore, although the principal focus of a Lens (as determined by the degree of its convexity) is always the same, yet the focus for objects near at hand constantly varies, being longer as they are brought closer to the Lens.

E. FORMATION OF A LUMINOUS IMAGE BY MEANS OF A LENS.

As the rays of light proceeding from a *point* are brought to a focus by means of a Lens, so are they when they proceed from an object, and in that case *an image of the object* is the result.



The above figure illustrates this. The arrow is reduced

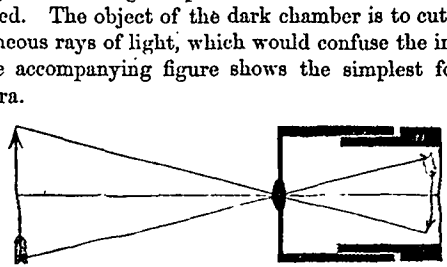
in size in proportion to its distance from the Lens; it is also *inverted*, as it necessarily must be, in obedience to the laws already laid down. In order that the reader may be able to see at a glance the course taken by the various pencils of rays as they fall upon the Lens, the lines from the barb of the arrow are *dotted*; observe particularly that all those rays which traverse the central point of the Lens, or the centre of the "axis" as it is termed, are not refracted, but pursue their original course as in the case of refracting media with parallel surfaces.

SECTION III.

The Photographic Camera.

The Photographic Camera, although, from motives of utility and convenience, its complexity is, usually speaking, somewhat increased, is in its essential nature an extremely simple instrument. It consists merely of a *dark chamber* of any kind, having an aperture in front in which a lens is inserted. The object of the dark chamber is to cut off all extraneous rays of light, which would confuse the image.

The accompanying figure shows the simplest form of Camera.



The body is represented as consisting of two portions which slide within each other; but the same object of lengthening out or shortening the focal distance may be attained by making the Lens itself movable. A luminous image of any object placed in front of the Camera is formed by means of the Lens, and received upon a surface of

ground glass at the back part of the instrument. When the Camera is required for use, the object is first *focussed* upon the ground glass, which is then removed, and a slide containing the sensitive layer inserted in its place.

The Field of the Camera.—The luminous image, formed upon the ground glass, is termed by Photographers "the Field of the Camera," and is spoken of as being *flat* or *curved*, *sharp* or *indistinct*, etc. All these peculiarities depend upon the nature and construction of the Lens which is employed to form the image. They will be treated of under the following heads:—A. Chromatic aberration.—B. Spherical aberration.—C. The use of stops.—D. Of the double combination lenses.—F. Variations between the chemical and visual focus in lenses not corrected for colour.

A. CHROMATIC ABERRATION.

By examining the field of a Camera, it is often seen that the image is not uniform in appearance, but exhibits fringes of prismatic colours which are plainly produced by a certain amount of *decomposition* of white light having taken place.

The outside of a biconvex lens is strictly comparable with the sharp edge of a prism, and therefore it must of necessity produce a certain amount of the "chromatic aberration."

Now it occurred at once to the acute mind of Sir Isaac Newton, on first investigating this subject, that the chromatic aberration of lenses would be very difficult to overcome; and therefore he advised, in the construction of powerful telescopes, that the use of *refracting* media should be altogether discarded, and the image be formed by *reflection* from the surface of concave mirrors. Since then, however, facts have been brought to light which have entirely altered the views of opticians on this point.

The physical fact of "Irrationality of Dispersion" ex-

plained in its application to the construction of Achromatic Lenses.—If we cut prisms from a variety of transparent substances of different refracting powers, the solar spectra which are produced by them will of course vary in length; the coloured spaces being most widely separated, and the whole spectrum being longest in the case of those prisms which refract light the most powerfully. The general rule is, that the more dense in structure, the stronger the refracting power of the medium. Other circumstances, however, independent of density, greatly affect the result; but these need not at the present time be alluded to.

The diagrams given below (fig. 1) show the appearance of two spectra produced by hollow prisms filled respectively with Oil of Cassia and Sulphuric Acid, the former liquid being remarkable for its refractive power.

Fig. 1.

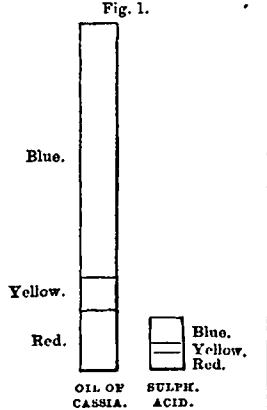
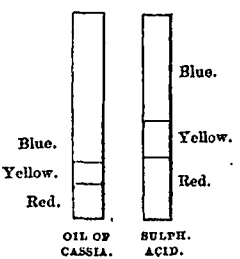


Fig. 2.



By a careful examination of these two spectra, however, it will be seen that a difference exists between them, altogether

independent of their comparative lengths, and of which nothing has yet been said. *The ratio between the spaces occupied by the elementary coloured rays* is not the same in both. The superior length of the Oil of Cassia spectrum seems to depend upon an abnormal extension of the blue-coloured space, whilst with the Sulphuric Acid the reverse obtains, and the red and yellow colours occupy more space in proportion to the total length than is usual.

In order that this *irrationality* of dispersion, as it is termed, may be fully understood, the two spectra have, in the second figure, been reduced to the same length, and it is at once seen that if they were applied to each other, face to face, the result would be to recombine the coloured rays, and so to produce again white light.

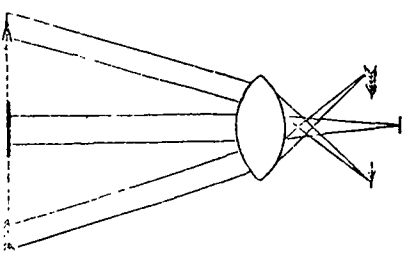
Means of constructing an Achromatic Lens.—The principle upon which an Achromatic Lens is formed is to combine two lenses, cut from varieties of glass which differ in their power of dispersing the coloured rays. These are the dense *flint* glass, containing much oxide of lead, and the light *crown* glass. Of the two lenses the one is *biconvex* and the other *biconcave*, so that when fitted together they produce a compound lens, which is a "meniscus." (See the diagram at page 76.)

In their passage through the biconvex portion of the Lens the rays are strongly refracted, and in the biconcave they are bent asunder again; consequently, on their emergence the complementary colours unite to a certain extent and reproduce white light.

The reader however is not to suppose that the difference in dispersive power between any two kinds of glass is at all to be compared with that shown in the diagram of the Oil of Cassia and Sulphuric Acid. So far from being so, it is very slight indeed: but practically it is sufficient for the purpose, a tolerably perfect coincidence of the complementary colours being all that is required.

B. SPHERICAL ABERRATION.

The various objects situate in the different parts of the field of a Camera cannot always be brought into perfect focus at the same time. If the centre part of the field is clear and distinct, then the outside is misty; whilst by moving the ground glass a little nearer to the Lens, so as to define the outside portion sharply, then the centre is found to be indistinct. Opticians express this by saying that there is a want of proper "flatness of field." This want of flatness is attributable in part to the "spherical aberration" of lenses,* that is, to the tendency observed in lenses which are segments *of spheres* to produce a *curved* image which does not admit of being received distinct in every part upon a flat surface. The following diagram will illustrate the formation of a curved image by a biconvex lens.†



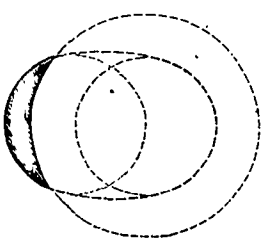
Observe that the rays which fall upon the circumference

* Curvature of the image is also caused by the oblique incidence of certain rays of light proceeding from the object, that is, from the fact of their not falling upon the lens *parallel to*, but *obliquely* with regard to the axis.

† This diagram is intended simply to illustrate the fact that the different portions of the lens possess different refractive powers; but it must not be taken to imply that the rays proceeding from the extremities of the arrow would correspond only to the outside of the lens, since it has already been shown in a previous diagram that such is not the case—that rays of light from every part of the object fall upon the whole circumference of the lens.

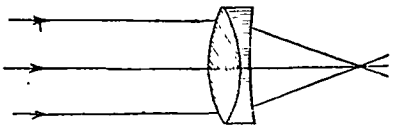
of the Lens are brought to a focus at a point nearer to the Lens than those passing through the centre. The cause of this is the same as that already shown to increase the chromatic aberration, viz. the greater inclination of the two surfaces of the Lens at the circumference than at any other part; hence, as it is at the *surfaces* of bodies that the deflecting power acts, it follows that the circumferential rays are more powerfully bent in than the central rays.

On the influence exerted on Spherical Aberration by the form of Curvature of the two surfaces of the Lens.—Spherical aberration of Lenses is overcome in a manner very different from chromatic aberration. Much in this respect depends upon the *form* of the lens, and it can be shown upon mathematical data that a lens similar to that given in the following diagram—one surface of which is a section of an ellipse, and the other of a circle struck from the furthest of the two foci of that ellipse—produces no aberration.



At the earliest period of the employment of the Camera obscura, a *Biconvex* Lens was used to produce the image; but this form was soon abandoned, on account of the spherical aberration so caused. Lenses for the Photographic Camera are now always ground of a concavo-convex form, or "meniscus," which corresponds more nearly to the above diagram.

The following figure shows the general form of outline of a Compound Achromatic Meniscus Lens.



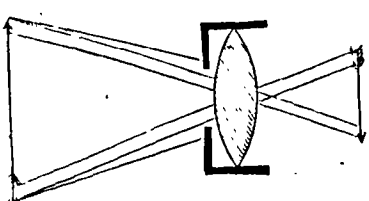
Observe also in this figure the division of the Lens into two distinct portions, for the purpose of obviating the chromatic aberration. The biconvex part of the Lens is the crown-glass; the biconcave, the flint-glass. Of the two the biconvex part is the most powerful, so as to overcome the other, and produce a total of refraction to the required extent.

C. ON THE USE OF "STOPS" IN LENSES.

As it has been shown that both chromatic and spherical aberration reside principally in the outside or circumferential portion of Lenses, the simplest remedy appears to be to cut off the outside and use only the central part of the Lens.

Now this is precisely what is effected by "a stop," which is a movable diaphragm, with a circular aperture, intended to be placed in front of the Lens in order to intercept that portion of the light which would otherwise have fallen upon the edge of the Lens.

The following diagram gives a sectional view of a Lens



with a stop fixed in front of it. It is seen that certain rays, proceeding from the arrow, are intercepted by the stop and proceed no further.

The employment of a stop is always attended with the disadvantage of cutting off a very large portion of the light, and so of diminishing the *brilliancy* of the image; it is never resorted to therefore in cases where a rapid action is desired; but when time of exposure is no object, a better result in very many ways is secured by the use of a stop.

Even supposing the Lens to be so carefully ground—which however it rarely is—that the spherical aberration is perfectly corrected, yet the *definition* or sharpness of outline of the image is improved. The various rays proceeding from the object, being confined to the centre portion of the Lens, interfere with and confuse each other less than they would otherwise do. They are made to fall upon the Lens at a higher and more equal angle, and therefore the distinctness of focus and flatness of field are proportionably improved.

From the same cause also it happens that when a stop of comparatively small diameter is used, a variety of objects, situated at different distances from the Lens, are all in focus at the same time; whereas, with the full aperture of the Lens, objects near at hand cannot be rendered distinct at the same time with distinct objects, or *vice versâ*.

D. ON THE DOUBLE OR PORTRAIT COMBINATION OF ACHROMATIC LENSES.

The brightness of illumination of any image formed by means of a Lens is always in proportion to *the diameter* of the Lens, that is, to the size of the aperture by which the Light is admitted.

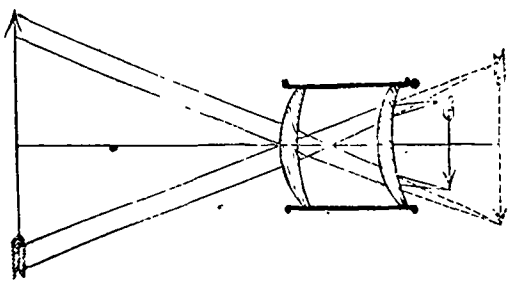
The *clearness or distinctness of outline* of the same image however is independent of the diameter, and indeed, as

has just been shown, is, usually speaking, *inversely* proportioned to it.

The use of a "stop" gives a distinct image, but feebly illuminated; whereas what the Photographer requires is an image combining both qualifications, that is, which shall be *clear* and *bright* at the same time.

The "double or portrait combination" effects this, and it is always employed when living objects, liable to move, are to be copied.

The following diagram is intended to explain the principle upon which the portrait combination is constructed.



Observe in this figure that two Lenses are employed, the second of which takes up the rays after their passage through the first, and refracts them still further. The dotted image marks the point at which the arrow would have been brought to a focus by the first Lens alone, and it is seen that the image actually formed is smaller and nearer to the Lens through the employment of the second glass. Now when an image is condensed and made smaller in this way, it is not only more bright in illumination, but it is also for the same reason very much sharper in the outline, so that the same effect as that resulting from use of a stop is obtained, although in another way.

The manufacture of Portrait Lenses is a point of great difficulty, and the glasses require to be ground with extreme care, in order to avoid *distortion* of the image. As the full aperture of both Lenses is employed, there is also much tendency to spherical aberration, and consequent want of flatness in the field of the Camera. The liability to both of these evils necessarily increases with the diameter of the Lenses, and the amount of condensation of the image, or shortness of the focus; hence the most rapid Portrait Lenses which are sold entail an amount of expense on the purchaser which few are able to encounter.

E. ON THE VARIATION BETWEEN THE VISUAL AND CHEMICAL FOCI IN CHROMATIC LENSES.

The same causes which produce chromatic aberration in a Lens, also tend to separate the chemical focus of the Lens from the visual focus.

The *blue*-coloured ray is more strongly bent in than the yellow, and still more so than the red; consequently the focus for each of those colours is necessarily at a different point. The following diagram shows this.

B represents the focus of the blue ray, Y of the yellow, and R of the red.

Now as the chemical action corresponds more to the blue, the most marked actinic effect would be found at B (or a little nearer to the Lens, the chemical rays being even more refrangible than the visible rays). The luminous portion of the spectrum however is not the blue, but *the yellow*, consequently the visual focus would be at Y.

Photographers have long recognized this point; and therefore, with ordinary chromatic Lenses—that is to say, Lenses which have not been corrected for colour—rules are laid down as to the exact distance which the sensitive plate should be shifted away from the visual focus, in order to obtain the greatest amount of distinctness of outline in the image impressed by chemical action.

These rules do not apply to the Achromatic Lenses recently described. The coloured rays being in that case bent together again and caused to reunite; the two foci also, nearly or quite, correspond.

It must be confessed however that our knowledge on this subject is at present incomplete, since it is not agreed by all as to whether the most rapid effects are produced by a Lens in which the actinic and luminous rays coincide, or whether the latter rays should be thrown slightly out of focus at the time of impression of the image; in other words, it is doubtful whether the *luminous* rays are simply *negative* in their action, or whether they exert a *positive retarding* effect upon the result. It is certain, at all events, that some Lenses are much quicker in action than others, —even independently of their focal length,—and that the cause of the difference in such cases cannot always be explained.

RECAPITULATION OF MAIN FACTS STATED IN THIS CHAPTER.

There are three principal ways in which white light may be decomposed into its elementary coloured rays, viz. by passing it through transparent bodies which are termed "coloured"; second, by *reflection* from the surfaces of opaque coloured bodies; third, by refraction through the angle of a prism.

Seven principal colours may be distinguished in the Solar Spectrum, but they are all reducible to three, viz.

blue, yellow, and red, the others being produced by the overlapping and intermingling of these.

The properties possessed by White Light may be divided into three classes—luminous, chemical, and heat-producing; each of these is associated with one of the primary colours in preference to the others: the blue is the chemical ray; the yellow, the ray producing vision; the red, the heating ray.

A Biconvex Lens condenses rays of light to a focus—a Biconcave Lens scatters them further asunder—a Meniscus combines both actions, the ultimate result depending upon the degree of curvature of the two surfaces.

Chromatic Aberration is caused by the Lens decomposing white light in the manner of a prism. It is corrected by cementing together lenses of opposite focal lengths and cut from distinct kinds of glass which vary in their dispersive power.

Spherical Aberration is a property possessed by Lenses *cut from spheres*, of refracting rays more powerfully at the circumferential than at the central part. It is corrected by substituting the "Meniscus" for the Biconvex Lens, and grinding the two surfaces according to certain fixed rules.

A Stop diminishes both chromatic and spherical aberration, by cutting off the outside portion of the Lens. It lessens the brilliancy of the image, but improves the distinctness by preventing various rays from interfering with and confusing each other; it also causes a variety of objects at different distances to be in focus at the same time.

A double combination of Lenses gives a highly condensed image, combining both brilliancy and distinctness; the Field of the Camera, however, is proportionably small, and usually deficient in flatness: distant objects and near objects cannot be focussed at the same time. The rapidity of action of the Lens increases with the diameter of the glasses and the shortness of the focus.

The visual and chemical foci usually correspond in an Achromatic Lens; but in an ordinary Lens not corrected for colour the latter is shorter than the former, *id est*, nearer to the Lens.

Lastly, the condition of light best fitted for photographic action cannot always be judged of by the apparent brightness of the atmosphere. The open sky is less favourable for reflecting light than a sky in which many thin fleeting clouds of a silvery hue are seen. In particular, certain invisible vapours in the upper regions of the atmosphere, by imparting a yellow tint to the light, often interfere with the actinic effect.

CHAPTER VII.

IODIDE OF SILVER UPON COLLODION.—CHEMISTRY OF THE SOLUTIONS CONCERNED IN ITS PRODUCTION.

In the preceding part of this work the physical and chemical properties of both Chloride and Iodide of Silver have been described, and the changes they experience by the action of Light sufficiently dwelt upon. Little or nothing, however, has been said of the importance of the surface intended to support these salts, and expose them in a finely divided state to the influence of the chemical radiations. This omission therefore will now be supplied, and *Collodion*, as a vehicle for Iodide of Silver, be introduced to the notice of the reader. The present chapter will include all that is known of the chemistry of the various solutions concerned in the production of the "Collodio-Iodide;" and the one which is to follow, its application to Photographic purposes.

The subdivisions of the chapter are four in number, viz.—I. The Chemistry of Plain Collodion; II. Of Iodized Collodion; III. Of the Nitrate Bath; and IV. Of the Collodio-Iodide film complete.

SECTION I.

Plain Collodion.

Collodion, so named from the Greek word κολλαω, *to*

stick, is a glutinous, transparent fluid, procured—as generally said—by dissolving Gun Cotton in Ether. It was originally intended to be used for surgical purposes only, being smeared over wounds and raw surfaces, in order to preserve them from contact with the air by the tough film which it leaves on evaporation. Photographers employ it to support a delicate film of Iodide of Silver upon the surface of a smooth glass plate.

Chemistry of Collodion.—Two elements enter into the composition of Collodion: first, the Gun Cotton; second, the fluids used to dissolve it. Each of these will be treated of in order.

A. CHEMISTRY OF PYROXYLINE.

Gun Cotton, or "Pyroxyline," as it will in future be termed, is Cotton or Paper which has been altered in composition and properties by treatment with strong acids.

Both Cotton and Paper are, chemically speaking, the same. The microscope reveals fibres which are found on analysis to have a constant composition. They contain three elementary bodies, Carbon, Hydrogen, and Oxygen, united together in fixed proportions; and to this combination the term "Lignine" (from *lignum*, wood) has been applied.

Properties of Lignine.—Cotton fibre, or Lignine, is a definite chemical compound, in the same sense as Starch or Sugar, and consequently, when treated with various reagents, it exhibits properties peculiar to itself. It is insoluble in most liquids, such as Water, Alcohol, Ether, etc., and also in dilute acids; but when acted upon by *Nitric Acid* of a certain strength it liquefies and dissolves.

It has been already shown, that when a body dissolves in Nitric Acid the solution is not, usually speaking, of the same nature as an aqueous solution would be; and so it happens in this case. The Nitric Acid does not take up

the Lignine *as Lignine*, but it imparts Oxygen first, and afterwards dissolves it.

Preparation of Pyroxyline.—If, instead of treating Lignine with Nitric Acid, a mixture of Nitric and Sulphuric Acids in certain proportions be used, the effect is peculiar. The fibres contract slightly, but undergo no other visible change. Hence we are at first disposed to think that the mixed Acids are ineffectual. This idea however is not correct, since on making the experiment we find that *the properties* of the cotton are widely different from what they were before. Its weight has increased by more than one-half; it has become soluble in various liquids, such as Acetic Ether, Ether and Alcohol, etc., and, what is most remarkable of all, it no longer burns in the air quietly, but *explodes* on the application of flame with greater or less violence.

This change of properties clearly shows, that although the fibrous structure of the Cotton is unaffected, it is no longer the same substance as at first, and consequently chemists have assigned to it a different name—that of "Pyroxyline."

Part played by each of the two Acids employed in the preparation of Pyroxyline.—To produce the peculiar change by which Lignine is converted into Pyroxyline both Nitric and Sulphuric Acids are, as a rule, required; but the distinctive part played by each of the two respectively is widely different. The former is by far the most important. On analysing Pyroxyline, Nitric Acid, or a body akin to it, is detected in considerable quantity, but not Sulphuric Acid. The Sulphuric Acid, in fact, serves but a temporary purpose, viz. *to prevent the Nitric Acid from dissolving the Pyroxyline*, which it would do if employed alone. The Sulphuric Acid seems to prevent the solution by removing water from the Nitric Acid, and so producing a higher degree of concentration; the Pyroxyline, although

it is soluble in a dilute, is not so in the strong acid, and hence it is preserved.

Illustration of the Attraction for Water possessed by Sulphuric Acid.—The property possessed by Oil of Vitriol of removing water from other bodies is one with which it is well to be acquainted. A simple experiment will serve to illustrate it. Let a small vessel of any kind be filled to about two-thirds with Oil of Vitriol, and set aside for a few days; at the end of that time, and especially so if the atmosphere be damp, it will have absorbed sufficient moisture to cause it to flow over the edge.

Now even the strongest reagents employed in chemistry contain, almost invariably, water in greater or lesser quantity. Pure Anhydrous Nitric Acid is a white, solid substance; Hydrochloric Acid is a gas; and hence the liquids sold under those names are merely *solutions*. The effect then of mixing strong Oil of Vitriol with aqueous Nitric Acid is to remove water in proportion to the amount used, and to produce a liquid containing Nitric Acid in a high state of concentration, and Sulphuric Acid more or less diluted. This liquid is the "Nitro-Sulphuric Acid," as it is termed, usually employed in the preparation of Pyroxyline.

Various Forms of Pyroxyline.—Very soon after the first announcement of the discovery of Pyroxyline, most animated discussions arose amongst chemists with regard to its solubility and general properties. Some spoke of a "solution of Gun Cotton in Ether," whilst others denied its solubility in that menstruum; a third class again, by following the process described, obtained a substance which was not explosive, and therefore could scarcely be termed Gun Cotton at all.

On further investigations some of these anomalies were cleared up, and it was found that there were *varieties* of Pyroxyline, depending mainly upon the degree of strength

of the Nitro-Sulphuric Acid employed in the preparation. Still the subject was obscure and encompassed with difficulty, until the publication of some researches by Mr. E. A. Hadow, of Bristol. These researches were conducted in the Laboratory of King's College, London, and afterwards communicated to the Journal of the Chemical Society. Constant reference will be made to them in the following remarks.

We notice—*first*, the chemical constitution of Pyroxyline; *secondly*, its varieties; and *third*, the means adopted to procure a Nitro-Sulphuric Acid of the proper strength.

a. *Constitution of Pyroxyline.*—It has been already said that Pyroxyline is found on analysis to contain Nitric Acid, or a substance akin to it. That such would be the case might have been imagined from the great increase of weight it was proved to have experienced. Is Pyroxyline then *a salt* of Nitric Acid—a "Nitrate of Lignine"?—for proper reasons chemists decide that it is not. Mr. Hadow proves, in the first place, that the substance present is not exactly Nitric Acid, but rather *the Peroxide of Nitrogen*, which, although it is sometimes termed *Nitrous* Acid, does not in reality possess any acid properties whatever, and is incapable of forming salts. Peroxide of Nitrogen has a composition similar to that of Nitric Acid *minus* one atom of Oxygen; it is NO_4 instead of NO_5. Pyroxyline then contains NO_4, or Peroxide of Nitrogen; but in order to understand properly in what state this body is combined with Lignine, it will be necessary to digress for a short time.

Law of Substitution.—By the careful study of the action of Chlorine, and of Nitric Acid, upon various organic substances, a remarkable series of compounds has been discovered containing a portion of Chlorine or of Peroxide of Nitrogen in the place of Hydrogen. The peculiarity of these substances is, that they strongly resemble the originals in their physical, and often in their chemical proper-

ties. It might have been supposed that agents of such active chemical affinities as Chlorine and Oxide of Nitrogen would, by their mere presence in a body, produce a marked effect; yet it is not so in the case before us. The primitive type or constitution of the substance modified remains much the same, even the crystalline form being often unaffected. It seems as if the body by which the Hydrogen had been displaced had stepped in quietly and taken up its position in the framework of the whole without disturbance. Many compounds of this kind are known; they are termed by chemists "substitution compounds." The law invariably observed is, that the substitution takes place *in equal atoms:* a single atom of Chlorine, for instance, displaces one of Hydrogen, and no more. But there are *successive steps* in the change, and hence a variety of products, each one containing less Hydrogen and more of the replacing body than the last.

In illustration of these remarks, take the following instances:—Acetic Acid contains Carbon, Hydrogen, and Oxygen; by the action of Chlorine the whole of this Hydrogen may be removed in the form of Hydrochloric Acid, and an equal number of atoms of Chlorine be made to take its place. In this way a new substance is formed, termed "Chloracetic Acid," resembling in many important particulars the Acetic Acid itself. Notice particularly that the peculiar properties characteristic of Chlorine are completely masked in the substitution body, and no indication of its presence is obtained by the usual tests! *A soluble Chloride* always gives with Nitrate of Silver a white precipitate of Chloride of Silver unaffected by acids, but the Chloracetic Acid does nothing of the kind; hence it is plain that the Chlorine exists in it in a peculiar and intimate state of combination different from what is usual.

The substance we have been previously considering, viz. Pyroxyline, affords another illustration of the Law of

Substitution. Omitting, for the sake of simplicity, the *number* of atoms concerned in the change, the action of concentrated Nitric Acid upon Lignine may be thus explained:—

$$\text{Lignine } or \begin{cases} \text{Carbon} \\ \text{Hydrogen} \\ \text{Hydrogen} \\ \text{Oxygen} \end{cases} + \begin{cases} \text{Nitrogen} \\ \text{Oxygen} \end{cases} or \text{ Nitric Acid}$$

equals

$$\text{Pyroxyline } or \begin{cases} \text{Carbon} \\ \text{Hydrogen} \\ \text{Peroxide Nitrogen} \\ \text{Oxygen} \end{cases} + \begin{cases} \text{Hydrogen} \\ \text{Oxygen} \end{cases} or \text{ Water}$$

In the case of the Chloracetic Acid the whole of the Hydrogen is displaced, but in the Pyroxyline a part always remains. It will be seen, by a reference to the formula, that the fifth atom of Oxygen contained in the Nitric Acid takes one of Hydrogen, and forms an atom of Water; the NO_4 then steps in, to fill the gap which the atom of Hydrogen has left. All this is done quietly and with so little disturbance that even the fibrous structure of the Cotton remains as before.

Chemical Composition of the Varieties of Pyroxyline.—Mr. Hadow has succeeded in establishing *four* different substitution compounds, which, as no distinctive nomenclature has been at present proposed, may be termed compounds *A*, *B*, *C*, and *D*.

Compound A is the most explosive Gun Cotton, and contains the largest amount of the Peroxide of Nitrogen. It dissolves *only in Acetic Ether*, and is left on evaporation as a white powder. It is produced by the strongest Nitro-Sulphuric Acid which can be manufactured.

Compounds B and C, either separate or in a state of mixture, form "the soluble cotton" of the Photographer. They both dissolve in Acetic Ether, and also in a mixture of Ether and Alcohol. The latter, viz. *C*, also dissolves

in glacial Acetic Acid. They are produced by a Nitro-Sulphuric Acid slightly weaker than the last, and contain a smaller amount of Peroxide of Nitrogen.

Compound D resembles what has been termed "Xyloidine," that is to say, the substance produced by acting with Nitric Acid upon Starch. It contains less Peroxide of Nitrogen than either of the others, and dissolves not only in Ether and Alcohol, but also in Acetic Acid. It is scarcely explosive.

By bearing in mind the peculiar properties of these several compounds, most of the anomalies complained of in the manufacture of Gun Cotton will disappear. If the Nitro-Sulphuric Acid employed is too strong, the product will be insoluble; whilst if it is too weak, the fibres will become matted together, gelatinized, and partly dissolved.

c. *Means adopted to procure a Nitro-Sulphuric Acid of the requisite strength for preparing Pyroxyline.*—This is a point of more difficulty than it would at first appear. It is easy to determine an exact formula for the mixture, but not so easy to hit upon the proper proportions of the acids required to produce that formula; and a very slight departure from them will altogether modify the result. The main difficulty is found in *the uncertain strength of commercial Nitric Acid.* Oil of Vitriol is more to be depended upon, and has a tolerably uniform Sp. Gr. of 1·836; but Nitric Acid is constantly liable to variation; hence it becomes necessary to make a preliminary determination of its real strength, which is done either by taking the specific gravity and referring to tables, or, better still, by a direct analysis. As each atom of Sulphuric Acid removes so much water and no more, it follows that the weaker the Nitric Acid, the larger the amount of Sulphuric which will be required in order to bring it up to the proper degree of concentration. Now in order to avoid the trouble necessarily attendant upon these preliminary ope-

rations, it is found convenient in many cases to substitute for the Nitric Acid itself *one of the salts formed by the combination of Nitric Acid with an alkaline base.* The *composition* of these salts, provided they are pure and nicely crystallized, can be depended upon for a certainty.

Nitrate of Potash, or Saltpetre, contains a single atom of Nitric Acid united with one of Potash. It is what is termed an *anhydrous salt*, that is to say, it has no water of crystallization. Now when strong Sulphuric Acid is poured upon this Nitrate of Potash in a state of fine powder, in virtue of its superior chemical affinities it appropriates to itself the Alkali and liberates the Nitric Acid. If care be taken to add a sufficient excess of the Sulphuric Acid, a solution is obtained containing Sulphate of Potash dissolved in Sulphuric Acid and free Nitric Acid. The presence of the *Bi*sulphate of Potash does not in any way interfere with the result, and therefore the effect is precisely the same as if the mixed acids themselves had been used.

The reaction may thus be represented:—

Nitrate of Potash *plus* Sulphuric Acid in excess
= Bisulphate Potash *plus* Nitro-Sulphuric Acid.

Recapitulation.—The chemistry of Pyroxyline, and of the materials employed to form it, having been sufficiently explained, we proceed to speak of its solution in the proper solvents. Before doing so, however, perhaps it will be well to insist once more on the fact, already stated, that Pyroxyline is, strictly speaking, *a neutral substance;* although it contains an element of such activity as the Peroxide of Nitrogen, yet nevertheless, being *a substitution compound*, its properties are masked and concealed. It is true that when heated, a violent explosion ensues, the compound being broken up, and the elements reuniting to form simpler bodies; but at common temperatures, Pyroxyline is very stable. As far as relates to its application to Photography,

in the present state of our knowledge, we must attribute the advantages gained rather to its physical properties than to its chemical composition.

B. CHEMISTRY OF THE SOLUTION OF PYROXYLINE IN ETHER AND ALCOHOL, OR "COLLODION" PROPERLY SO CALLED.

The substitution compounds B and C, already alluded to as forming the Soluble Cotton of Photographers, are both abundantly soluble in Acetic Ether. This liquid however is not adapted for the purpose required, inasmuch as on evaporation it leaves the Pyroxyline in the form of a white powder, and not as a transparent layer.

The rectified Ether of commerce has been found to answer better than any other liquid as a solvent for Pyroxyline.

This "Sulphuric Ether," as it is called, always contains a small portion of *Alcohol*, which appears to be necessary; the solution scarcely taking place at all with absolutely pure Ether. When treated, then, with this rectified Ether, the Cotton, if properly prepared, begins almost immediately to gelatinize, and is soon completely dissolved. In this state it forms a slimy solution, which, when poured out upon a glass plate, speedily dries up into a horny transparent layer.

Collodion therefore is a solution of one or more of the varieties of Pyroxyline in a mixture of Ether and Alcohol.

Now in making use of Collodion for photographic purposes, we soon find that its physical properties are liable to considerable variation. Sometimes it appears to be very thin and fluid, flowing over the glass almost like water, whilst at others it is thick and glutinous. The causes of these differences will now engage our attention. They may be divided into two classes—first, those relating to the soluble cotton; second, to the solvents employed.

a. *Variation in properties observable in different samples of Soluble Cotton.*—Pyroxyline appears in some cases to be an exception to the usual chemical law, that when two bodies are the same in *composition*, they are the same in properties also. We can understand what has already been stated with regard to the compounds A, B, C, and D. Each of these contains a different amount of the replacing body, Peroxide of Nitrogen, and therefore we are not surprised to find that some are more explosive and insoluble than others; but it often happens in the preparation of soluble Cotton that a definite Nitro-Sulphuric Acid will yield in two different experiments products varying in their solubility.

A practical Photographer, who has had much experience in the preparation of Pyroxyline, will probably have noticed that there are two principal modifications of that substance, possessing the following general characteristics.

The first dissolves in a mixture of Ether and Alcohol to a considerable extent, and forms a very fluid solution. When poured on a glass plate it quickly spreads out into a beautifully smooth and glassy surface, in which no ridges or inequalities of any kind can be detected.

The second variety dissolves in the Ether as readily as the first, but the solution when formed is of a different nature: it is thick and glutinous, and not fluid as before. When poured out it flows along in a slimy manner, and soon sets into numerous small waves and cellular spaces. On adding more Ether, or Alcohol, or both, for the purpose of thinning it down, the evil is lessened, but not altogether removed, so that at length the operator is compelled to lay it aside in despair.

The description here given applies to the *extremes* in each case, and oftentimes compounds result which possess intermediate properties.

Explanation of the Causes of these Differences, so far as

they have been ascertained.—It has already been stated that the variation in properties is independent in great measure of chemical composition,—that two samples may differ much in these minor points, which agree perfectly on analysis.

Mr. Hadow has pointed out clearly *one cause* of the difference, viz. *the temperature of the Nitro-sulphuric Acid* at the time of immersing the Cotton. The first or soluble variety is produced by *warm* acids; the second, or "glutinous," by the same acids employed cold. The best temperature appears to be about 130° or 140° Fahrenheit, and if it rises much beyond that point the acids soon act upon and dissolve the Cotton. The practical inconvenience resulting from a previous lack of information on this point had been the less felt, because *the mere mixture* of the two acids, or of the Sulphuric Acid and Nitre, will often produce the requisite degree of heat.

However, there are beyond doubt other causes, besides the one just mentioned, and which still remain to be investigated. Even a *warm* mixture of acids will occasionally produce a glutinous product. It seems also that Pyroxyline obtained from the Swedish filtering paper is less liable to vary in solubility than that prepared from Cotton wool; also there is reason to think that *a very prolonged digestion* in the acid mixture, in the case of Cotton wool, is apt to injure the resulting Pyroxyline, as far as ready-flowing qualities of the solution are concerned.*

b. *Physical properties of Collodion as affected by the Condition of the Solvents employed.*—Collodion wool, as be-

* Since the above was written the Author has tried the effect of "Chloroform" in removing the glutinosity of some samples of Collodion, as suggested by Mr. Shadbolt, and finds it to succeed. That it should do so is the more remarkable, because Chloroform does not dissolve Pyroxyline, and the first effect of adding it to the Collodion is to precipitate a portion of that substance in the form of jelly-like masses. These however redissolve on shaking, and the solution eventually becomes more fluid than before.

fore said, is not soluble either in Ether, or in Alcohol, employed alone; but it dissolves readily in a mixture of the two fluids. The characters of the resulting solution differ somewhat according to the relative proportions of Ether and Alcohol employed, and also with the presence or absence of "water" in one or both of these liquids.

1. *Relative Proportions of the Solvents.* — Supposing both Solvents to be perfectly pure, the Pyroxyline dissolves freely until the proportions reach to about equal parts of Ether and Alcohol. The further addition of Alcohol, after that point, renders the fluid somewhat thick and glutinous.

The physical properties of a Collodion however differ in some respects according to the relative proportions of the Ether and Alcohol.

When the Ether is in large excess the film is strong and tough, so much so that it can often be raised by one corner and lifted completely off the plate without tearing. Also it is *very contractile*, so that if a portion of the Collodion be poured on the hand it draws together and puckers the skin as it dries. If it is spread upon a glass plate in the usual way, the same property of contractility often causes it to retract and separate from the sides of the glass.

These then are the properties of the film caused by Ether in excess; on addition of Alcohol in some quantity they disappear entirely. The transparent layer is now soft and easily torn, possessing but little coherency. It adheres to the surface of the glass very firmly, and exhibits no tendency to contract and separate from the sides. All these qualities are favourable to its employment by the Photographer.

2. *Physical properties of the Collodion affected by the presence of Water in the Solvents.*—If a few drops of water be purposely added to a sample of Collodion, the effect is seen to be to precipitate the Pyroxyline in flakes

to the bottom of the bottle. There are many substances known in chemistry which are soluble in spirituous liquids, but behave in the same manner as Pyroxyline in this respect.

The manner in which water is apt to gain entrance into the Photographic Collodion is, usually speaking, by the employment of Alcohol or Spirits of Wine which has not been sufficiently highly rectified. Spirit and Water mix in all proportions, and the object of rectification is to strengthen the Spirit by the separation of Water.

The injurious effects produced by water when present *only in small quantity* are not very evident. The Collodion is somewhat thicker, and flows less readily than it would have done if the Alcohol had been stronger. A further addition however is followed by worse results: *the texture of the film left upon evaporation is injured.* It is no longer homogeneous and transparent, but semi-opaque and *reticulated;* made up entirely of a network of small fibres enclosing spaces, and so rotten that a stream of water projected upon the plate washes it away.

These effects are to be attributed not to the Alcohol, but to the Water which was introduced with the Alcohol; and the remedy is to procure a stronger spirit, or, if that cannot be done, to increase the proportion of Ether in the Collodion.

SECTION II.

Iodized Collodion.

In a former chapter, whilst speaking of the development of a latent image by means of a reducing agent, it was shown that the Iodide of Silver was better adapted to the purpose than the Chloride, not only as being a more sensitive preparation, but also as withstanding the action of the developer better in those parts not exposed to light; con-

sequently the Collodio-*Iodide* of Silver will at present alone engage our attention. The present section treats of all that relates to the Iodized Collodion; and the one which follows, to the Nitrate of Silver solution.

In order to produce the Collodio-Iodide of Silver, the plan always adopted is to select an Iodide of some kind which is soluble in a mixture of Alcohol and Ether, and to add a portion of this to plain Collodion. Afterwards a plate of glass is coated with a layer of the "Iodized Collodion," and whilst it is "setting"—in a state neither wet nor dry—it is immersed in a solution of Nitrate of Silver, and allowed to remain until the decomposition is complete.

The points of interest are these—the nature of the Iodide best adapted to the purpose, and the chemical changes which Iodized Collodion undergoes by keeping.

A. NATURE OF IODIDE BEST FITTED FOR IODIZING COLLODION.

The Iodides of Potassium, Ammonium, and Cadmium have all been employed for the purpose of iodizing Collodion, and each one has had its respective advocates. Theoretically speaking, it seems a matter of indifference which is preferred.* In each case Iodide of Silver is alike produced, with a portion of neutral salt, Nitrate of Potash or Nitrate of Ammonia, and there is no reason to suppose that this neutral salt in any way affects the result. The Author found by experiment that if the Iodides used were chemically pure and the Collodion new and colourless, no difference could be detected either in sensitiveness or perfection of half-tones.

* For some remarks tending to qualify this statement, see Part II. Chapter II. Section I.—foot-note to Formula for Collodion.

Iodide of Potassium.—This salt is more sparingly soluble than the others, and indeed the quantity considered by many to be requisite cannot be made to dissolve in Ether and Alcohol perfectly free from Water. However, as Iodide of Potassium is easily obtained pure, and is a comparatively stable substance, it forms a good basis for iodizing.*

Iodide of Ammonium.—This dissolves in the ethereal mixture more readily than the Potassium salt, but it has the disadvantage of being exceedingly apt to decompose by keeping. It becomes brown from liberation of free Iodine, and is then unfit for use.

Iodide of Cadmium.—This is a beautifully crystalline and very stable salt, easily obtained in a state of purity, and very soluble in Alcohol and Ether. Iodide of Cadmium possesses some peculiarities as an "iodizer" which distinguish it from the alkaline Iodides; they will be alluded to more fully in the latter part of this Section.

Double Iodide of Potassium and Silver.—The general nature of this compound salt has been sketched at page 21. It is however, at the present time, but rarely employed in iodizing Collodion.

B. CHEMICAL CHANGES EXPERIENCED BY IODIZED COLLODION ON KEEPING.

Iodized Collodion, when first prepared, is perfectly colourless if the materials employed were pure. It does not however long remain so, but begins to change by degrees to a lemon-yellow colour, afterwards to an orange-yellow, and finally to a dark red.

These effects are due to the liberation of *free Iodine*,

* For the preparation, etc., of Iodides used in the manufacture of Collodion, see Part II. Chapter I.

which, usually speaking, can be detected in the solution by its appropriate tests.*

This liberation of Iodine is produced by the *Ether* rather than by the other constituents of the Collodion. Not that this fluid produces any such result when perfectly pure, but that it is liable to have its properties changed by gradual decomposition.

It is common amongst Photographers to say that the effect is due to slight *acidity* of the Ether; the simple fact of acidity however does not altogether explain the phenomenon. The tendency of ordinary acid placed in contact with Iodide of an alkali is to set free, not Iodine, but *Hydriodic Acid*—that is to say, Iodine in combination with Hydrogen (HI); and although Hydriodic Acid is an unstable substance and soon becomes decomposed, yet it does not do so sufficiently quickly to strike an immediate colour.

There are indeed certain acids which eliminate Iodine exceedingly rapidly from the Iodide of Potassium, viz. those which contain *oxygen loosely combined*, as for instance the Nitric Acid, or, better still, the same saturated with the red vapours of Peroxide of Nitrogen. Peroxide of Nitrogen and Hydriodic Acid instantly react upon each other with formation of Water and free Iodine, thus:—

$$HI + NO_4 = HO + I + NO_3.$$

Some have thought that the colouration of Iodized Collodion is in all cases to be explained in this way—that a portion of the Pyroxyline suffers decomposition, and that Peroxide of Nitrogen is set free.

This may be the case possibly to a certain extent, but it does not altogether explain the facts, because the same co-

* The Author finds that the delicacy of the "starch test" is much interfered with by the presence of *Alcohol*, and that a quantity of Iodine, which in solution in water strikes a deep blue, cannot be detected when dissolved in spirit.

louration takes place, although more slowly, in a solution from which the Pyroxyline is omitted.

No investigations appear to have been made upon the precise nature of this peculiar compound existing in Ether, but it is produced in either of the following ways:—

a. *By exposing Ether to the joint action of air and light.*—After a time the fluid assumes a distinct acid reaction, which is probably due to Acetic Acid.

b. *By long keeping.*—A portion of Ether, which was originally free from it, acquired the property of liberating Iodine, after having been kept for six months. In this case the action of air and light had been excluded, but the change, although delayed, was not thereby altogether prevented.

c. *By introducing a red-hot wire into a bottle containing the vapour of Ether mixed with air.*—In this case a considerable development of the principle takes place; the rapidity of the oxidation is probably hastened by the elevation of temperature.

Mode in which Ether may be freed from this peculiar principle.—Mere washing with water does not suffice, but redistillation from a caustic Alkali appears to answer the purpose effectually.

The colouration of Iodized Collodion as affected by the nature of the Iodide employed.—Some Iodides are decomposed by Ether more easily than others; Iodide of Ammonium, for instance, colours more quickly than Iodide of Potassium, whilst the Iodide of Cadmium scarcely colours at all. This fact was first pointed out by Mr. Hadow, who does not however attempt to explain it.

Further changes in the composition of the Collodion caused by the gradual reaction of the Iodine upon the Ether.—This subject requires to be further studied. Collodion only slightly tinted with Iodine regains its original properties if the Iodine be removed; but it is doubtful

how far this is the case when the colouration has been extensive, and time allowed for further changes to ensue.

Löwig has examined the effects of "Bromine" upon Ether, and finds the fluid is decomposed gradually with production of Hydrobromic Acid, Hydrobromic Ether, Bromal and Formic Acid. Possibly in the case of Iodine the change may be analogous, but less strongly marked, the chemical affinities of that element being weaker than those of Bromine.

Simple process for removing the liberated Iodine.—The amount of free Iodine required to produce a lemon-yellow colour is so excessively small, that it can scarcely be said to produce an appreciable effect in a Photographic point of view. When the tint however reaches to an orange or red colour, it may be desirable to remove it. This may be done by adding a small portion of a caustic Alkali, such as Potash or Ammonia, but better still by the simple and ingenious plan proposed by Mr. Crookes,—placing a piece of silver foil in the bottle containing the Collodion, and allowing it to remain as long as required. Iodide of Silver is first formed, which afterwards dissolves in the alkaline Iodide. A strip of metallic Zinc likewise produces the same effect of decolourizing Collodion.

SECTION III.

The Nitrate Bath.

The solution of Nitrate of Silver in which the plate coated with iodized Collodion is dipped, in order to form the layer of Iodide of Silver, is known technically as "*the Nitrate Bath.*" The proper management of it is one part of the knowledge required in a practical Photographer. At present we notice the following points connected with the Chemistry of the Bath, viz.—A, its property of dissolving a certain portion of Iodide of Silver; B, the changes

34100

it undergoes by exposure to the light; C, acidity of the Nitrate Bath; D, alkalinity of the Nitrate Bath.

A. PROPERTY POSSESSED BY NITRATE OF SILVER OF DISSOLVING IODIDE OF SILVER.

Nitrate of Silver was mentioned in the second Chapter in the list of solvents of the Iodide of Silver. The proportion dissolved is in all cases very small, but it increases with the strength of the solution. If no attention were paid to this point, and the precaution of previously saturating the Nitrate Bath with Iodide of Silver neglected, although the film would be produced equally well at first, yet it would be liable to be afterwards attacked and dissolved away.

This solvent power of Nitrate of Silver on the Iodide of Silver is well shown by taking the excited Collodion film out of the Bath, and allowing it to dry spontaneously. The layer of Nitrate on the surface becomes concentrated by evaporation, and eats away the film in parts, so as to produce a transparent, spotted appearance.

In the solution of Iodide of Silver by Nitrate of Silver a *double salt* is formed, which corresponds somewhat in properties to the double Iodide of Potassium and Silver, that is to say, it is *decomposed* on the addition of water. Consequently, in order to saturate a Bath with Iodide of Silver, nothing more is necessary than to dissolve the total weight of Nitrate of Silver in a small bulk of water, and to add to it a few grains of Iodide of Silver. Perfect solution takes place, and on subsequent dilution with the full amount of water, the excess is precipitated in the form of a milky deposit.

B. CHEMICAL CHANGES IN THE BATH PRODUCED BY EXPOSURE TO LIGHT.

Pure solution of Nitrate of Silver is not affected by

the action of light. The Nitrate Bath however, although pure at first, does not long continue to be so. Each time a coated plate is dipped, *organic matter* in the shape of Alcohol and Ether is introduced. This organic matter, in conjunction with the light, soon reacts upon the Nitrate of Silver, and causes a brown deposit which settles in small quantity at the bottom. The deposit is metallic Silver, and it is produced by a regular process of reduction, Oxygen being separated, and combining with the reducing agent in the usual manner. If a careful analysis of the Bath be made after a certain time, probably *Acetate* and *Nitrite* of Silver will be detected. The former is produced by the oxidation of Alcohol or Ether into Acetic Acid, and the latter is the first stage of reduction of Nitrate of Silver.*

The properties of the solution, as will be hereafter seen, are materially affected by these changes in its composition, and hence it is necessary to bear in mind that the Nitrate Bath *must be kept carefully excluded from the light.*

Probably there are other effects besides those above mentioned, produced by the continued action of Light upon the Bath. Some time since a Bath was placed in the hands of the Author for analysis, which yielded on distillation a volatile organic substance possessing curious properties. It had a peculiar smell distinct from that of either of the constituents of Collodion, and when added to a pure solution of Nitrate of Silver, caused a universal decomposition of the film of Iodide of Silver under the influence of the developing agent.

C. ACIDITY OF THE BATH.

The Photographic properties possessed by a Nitrate Bath

* A Nitrate Bath containing Alcohol, having been exposed for a long time to the diffused light of day, deposited long needle-crystals precisely resembling Nitrite of Silver in appearance, whilst at the same time it began to yield very sensitive films of Iodide of Silver. (For the Nitrites, see Part III.)

vary much accordingly as the solution is in an acid or neutral state. At present we confine ourselves to an explanation of the manner in which *acidity of the Bath* is caused, leaving its Photographic peculiarities until another occasion. *Pure Nitrate of Silver* is neutral to test-paper, but the Nitrate sold in the shops has mostly an acid reaction. This arises from the fact that the crystals have been imperfectly drained from the acid mother-liquor in which they were formed. Hence, in making a new Bath it is necessary not only to saturate it with Iodide of Silver, but to neutralize the free acid it contains.

Supposing the Nitrate Bath however to have been perfectly neutral when recently prepared, it very shortly becomes *acid* by continual use. The acidity in this case is caused by the employment of Collodion containing *free Iodine*, in which case a portion of Nitric Acid is liberated each time the plate is immersed in the Bath, thus:—

Nitrate of Silver + Iodine
= Iodide of Silver + Nitric Acid + Oxygen;

or in symbols,

$$AgO\,NO_5 + I = AgI + NO_5 + O.$$

Observe that not only Nitric Acid but also *an atom of Oxygen* is set free by the Iodine. How far this influences the result, it is not easy to say; but probably, being in the nascent state, it immediately combines with organic matter and is removed out of the way. Practically speaking, it is useful to bear in mind that free Iodine in the Collodion is equivalent to free Nitric Acid in the Bath, and that the effect of constant use will be to render the solution more and more contaminated with Nitric Acid, unless care is taken to remove it.*

* These remarks do not apply if *Acetate* of Silver has been added to the Bath, as will by-and-by be recommended. In that case free Iodine in the Collodion corresponds to free *Acetic* Acid after dipping the plate.

D. ALKALINITY OF THE BATH.

By alkalinity of the Bath is meant a condition in which the blue tint is restored to reddened litmus-paper. Such a fact indicates that *a metallic Oxide* of some kind is present in solution, which, by combining with the acid in the reddened paper, neutralizes it and removes the red colour.

If a small portion of caustic Potash or Soda be added to a strong solution of Nitrate of Silver, it speedily produces a brown precipitate, which is the Oxide of Silver. The solution however, from which the precipitate has separated, is not left in a neutral state after such addition, but possesses an alkaline reaction.

This effect is caused by a *minute* quantity of the Oxide of Silver, which is displaced by the stronger oxide, Potash, dissolving in the liquid. For all practical purposes Oxide of Silver may be said to be insoluble in water; but after precipitation a trace always remains, and probably the quantity dissolved becomes larger if the water holds Nitrate of Silver in solution.

Oxide of Silver and Carbonate of Silver are also *abundantly* soluble in water containing *Nitrate of Ammonia;* and as this salt is continually accumulating in the Bath, when compounds of Ammonium are used for iodizing, it is well to bear such a fact in mind.

The production of Nitrate of Ammonia by use of Collodion containing Iodide of Ammonium is thus shown.

Iodide of Ammonium + Nitrate of Silver.
= Nitrate of Ammonia + Iodide of Silver.

Now Alkalinity of the Bath is a most pernicious condition, photographically considered; and therefore it will be well to lay down the following rules in order to avoid it.

1st. Never to employ a Collodion containing free Ammonia or Carbonate of Ammonia. If such is done, Oxide and Carbonate of Silver are formed at every dip of the

plate, and after a time a distinct alkaline reaction is produced.

2nd. In attempting to neutralize a Bath which contains free Nitric Acid,—after the addition of the Carbonate of Soda—which perhaps is as good an agent for the purpose as any other—to test for alkalinity, and if any is discovered, to add *a single drop* of Acetic Acid, and then test again: the fact of one drop of Acetic Acid (glacial) often sufficing to neutralize the whole of the Carbonate of Silver dissolved in a Bath of perhaps eight ounces or more, shows how sparing is the solubility of this salt; nevertheless even that minute quantity is enough to produce injurious effects.

The alkalinity of a Nitrate Bath has been sometimes erroneously attributed to the presence of small quantities of Potash or Ammonia, but it is contrary to all the received laws of chemistry that this should be the case. Both Potash and Ammonia are more powerful in their chemical affinities than Oxide of Silver, and therefore on coming in contact with Nitrate of Silver they displace that substance; thus—

Ammonia + Nitrate of Silver
= Oxide of Silver + Nitrate of Ammonia.

SECTION IV.

The Collodio-Iodide Film complete.

Having explained the chemistry of the solutions required to form Collodio-Iodide of Silver, as far as is at present necessary, we proceed to the physical properties of the film itself, as prepared ready for the Camera.

Now there are a variety of circumstances which modify the *appearance* and general characters of this film, some of which are as follows:—the strength of the solutions employed in its formation; the time allowed to elapse before and during immersion in the Bath, etc. etc.

A. RELATIVE AND ABSOLUTE QUANTITIES OF ALKALINE IODIDE AND OF NITRATE OF SILVER.

A proper relation should always be observed between the proportion of Alkaline Iodide in the Collodion, and of Nitrate of Silver in the Bath. If the latter salt fall below a certain point in reference to the first, the decomposition will be incomplete, the liquid imbibed by the porous film not containing enough Silver for the purpose.

Supposing however the relative proportions to be correct, yet much depends upon the absolute quantities of both salts;—in other words, the appearance of a Collodio-Iodide film varies in accordance with the amount of Iodide of Silver it contains. As these differences much affect the photographic peculiarities, they will be described somewhat minutely.

When the proportion of Iodide of Silver is small, the film will be found on immersion in the Bath to assume by degrees *a pale blue opalescent tint*, which on inspection is found to be transparent to such an extent that the letters of a newspaper can be read through it at a distance of some inches with facility.

By slightly increasing the quantities, the blue film is found to have changed to a silver-grey, still transparent, but less so than before.

The next stage is a tendency to yellow, with comparative opacity; and higher still, a decided creamy, yellow, and opaque film.

When this point is reached, no further alteration in appearance is produced by adding more Iodide; but eventually it is found that flakes of Iodide of Silver burst out upon the surface of the film and fall away into the Bath. When this is the case, the Collodion is decidedly over-iodized, and the result will be inferior in every respect.

B. TIME ALLOWED TO ELAPSE BETWEEN COATING THE PLATE WITH COLLODION AND IMMERSING IT IN THE BATH.

It has been already said that a Collodion layer when poured on the glass plate is not to be allowed to become *perfectly dry* before it is immersed in the solution of Nitrate of Silver.

After exposure to the air for a short time, the greater part of the Ether evaporates, and leaves the Pyroxyline in a state in which it is neither wet nor dry, but receives the impression of the finger without adhering to it. Photographers term this "*setting*," and when it takes place it is a sign that the proper time has come for submitting to the action of the Bath.

If the film is lowered into the Nitrate before it has set, the effect is somewhat the same as that already described as produced by adding *Water* to Collodion. The Pyroxyline is precipitated more or less, and consequently the after-structure of the film is not homogeneous. On the other hand, if it is allowed to become too dry, the Iodide of Silver does not form perfectly, and the film, on being washed and brought out to the light, exhibits a peculiar iridescent appearance, and is paler in some parts than in others.

No rule can possibly be given as to the exact time which ought to elapse: it varies with the temperature of the atmosphere, and with the proportions of Ether, and of Pyroxyline.

C. TIME OF IMMERSION IN THE BATH.

After the plate has been lowered into the Bath, it must be allowed to remain until the conversion of the Alkaline Iodide into Iodide of Silver is complete.

The principal impediment in this part of the process lies

in the difficulty with which Ether and Water mix together; this causes the Collodion surface on its first immersion to appear *oily* and covered with streaks. By gentle motion the Ether is soon washed away, and a smooth and homogeneous layer obtained.

D. PHYSICAL CHARACTERISTICS OF A PERFECT FILM.

It is never advisable to employ a sample of Collodion without having previously examined the physical structure of the film of Iodide of Silver which it yields. In this way we are able to judge of its Photographic qualities with tolerable accuracy, and also frequently to save subsequent disappointment by detecting causes of failure at an early period.

The characteristics of a perfect film—as seen after washing with water and bringing out to the light—are these:—

It presents a very smooth and uniform appearance, both by reflected and transmitted light, being of equal thickness in every part; there are no wavy lines or spaces such as would be caused by a glutinous Pyroxyline; no *opaque dots* from small particles of dust or Iodide of Silver in suspension in the Collodion.

The evidences of a *too rapid immersion in the Bath* are to be sought for on the side of the plate from which the Collodion was poured off. This part necessarily remains wet longer than the other, and hence it always suffers the most; horizontal cracks or marks resembling vegetation are seen, each one of which would cause an irregular action of the developing fluid used in the after processes. On the other hand, *the upper part* of the plate, and not the lower, is the place to examine for signs of the film having been permitted *to become too dry* before immersion, since the Collodion film is thinner at that point than at any other.

CHAPTER VIII.

IODIDE OF SILVER UPON COLLODION, CONTINUED.—PHOTOGRAPHIC PROPERTIES OF THE COLLODIO-IODIDE.

It is intended to establish a division of this Chapter into six Sections. The first of these will treat of the causes influencing the *sensitiveness* of the Collodio-Iodide of Silver; and the second, of the development of the latent image. Afterwards, some general remarks will be made relating to both of these subjects combined, which will form the contents of the four remaining Sections.

Now there can be no doubt but that the action of the light and that of the developing fluid are, as far as all practical purposes are concerned, very closely associated; and on taking a finished Photograph in the hand, it requires considerable experience to enable us to say immediately how much of the effect was produced by each of the two agents separately, or, if there is a fault, to which it is to be attributed.

Nevertheless it is thought that by a careful study of the various reactions involved in the process, much may be done, and that with care the impression of the image by the light may be distinguished, to a certain extent, from its subsequent development.

Two terms will be made use of so frequently, that it is esssential to begin by laying down the sense in which they are to be understood.

These terms are "Sensitiveness" and "Intensity." By "sensitiveness" is meant a facility of receiving impression from very feeble rays of light, or of receiving it *quickly* from more energetic rays.

Intensity, on the other hand, relates to the appearance of the finished Photograph, independently of the time taken to produce it; *to the degree of opacity of the reduced Silver*, and the extent to which it obstructs transmitted light.

Now with the intensity of a picture, as will be seen by-and-by, the developing fluid is largely concerned; but with "sensitiveness" it has but little to do, since the most powerful reducing agent cannot be made to bring out an image the details of which have not been properly impressed by Light.

SECTION I.

Causes influencing the Sensitiveness of the Collodio-Iodide of Silver.

The student is already acquainted with the principal phenomena of the production of a latent image, and with the chemical changes concerned in its subsequent development by means of a reducing agent.

No attempt however has been made to explain minutely the action of the light, which can only be done by degrees, as our knowledge of the subject increases.

Probably the idea at first conceived, from observation of experiments made upon paper, would be that the light and the developing agent worked together: the latter continuing the action begun by the former, and bringing it to a more rapid conclusion.

This however is not altogether the case, as will soon be seen.

If the nature of the effect produced by the developer were the same in kind as that of the Light, and differed from it only *in degree*, it is obvious that either could be made to take the place of the other indifferently,—that, for instance, a picture exposed unusually long, and therefore in which the reduction by light was carried further, would be developed with unusual ease. So far from this theory being true, it can be shown that the effect of prolonged exposure is injurious rather than otherwise; that the light, after a certain time, attains its maximum, and proceeds no further.

At present, then, we bear in mind that the action of light upon the film is *a definite action* of some kind peculiar to itself, and not admitting of comparison beyond a certain point with that of the developer.*

Some of the causes which affect the sensitiveness of the Collodio-Iodide of Silver are as follows:—A. The proportions of Ether and Alcohol in the Collodion employed.—B. Free acid in the film.—C. Excess of Nitrate of Silver in contact with the Iodide of Silver.—D. Proportion of Iodide of Silver contained in the film.—E. Addition of bodies in a state of change and tending to absorb oxygen.—F. Temperature and other causes imperfectly studied.

Many of these same conditions however also produce other effects upon the film, besides modifying its sensitiveness; but as these involve the process of development as well as the action of the light, they will be treated of in separate Sections.

* The further consideration of this subject is postponed to Section III. The arguments to be adduced in favour of certain hypotheses presuppose a knowledge of the developing process, which has not as yet been explained. For the same reason a separate Section (viz. Section IV.) is devoted to a discussion of the most probable causes of the excessive sensitiveness of the Collodio-Iodide of Silver.

A. RELATIVE PROPORTIONS OF ETHER AND ALCOHOL EMPLOYED IN THE COLLODION.

This has already been alluded to, as far as the *physical properties* of the solution are concerned. It has been shown that an increase in the amount of Alcohol lessens the contractility of the film, causes it to adhere more firmly to the glass, and facilitates the production of the sensitive layer of Iodide in the Bath.

As the physical qualities of the film are altered by addition of Alcohol, so also are its Photographic qualities. It is rendered far more sensitive to the influence of light, the image being impressed in a shorter time than before. Therefore the rule has always been to add as much Alcohol to the Collodion as it will bear, the exact quantity depending upon the strength of the spirit, that is to say, its freedom from dilution with water.

The good effects produced by Alcohol must be referred mainly, not to a chemical, but to a *mechanical* cause. The structure of the film is opened out, as it were, and being less dense and compact the Iodide is better acted upon by the Light.

B. FREE ACID IN THE FILM DURING EXPOSURE TO LIGHT.

This retarding cause is placed early on the list on account of its importance.

When we speak of "Collodio-Iodide of Silver," we suppose all the conditions to be chemically neutral; neutral Iodide of Silver in contact with neutral Nitrate of Silver. In practice however this perfect neutrality is very seldom obtained; either the Nitrate Bath is faintly acid, or the Collodion is brown from free Iodine, both of which causes tend to produce an acid film. There are certain advantages—as far as *clearness* of image is concerned—in using an acid film, but of these we do not now speak; what we

notice at present is that acids of all kinds diminish the sensibility, and render necessary a longer exposure to light.

Some acids produce this effect in a much greater degree than others; especially so acids *possessing oxidizing powers;* thus *Nitric Acid* is a powerful retarding agent, whilst Acetic Acid, being a more feeble body, is less injurious in that respect.

The structure of the film is another point to which attention must be paid. The less the quantity of Iodide of Silver, and the more slight and transparent the film, the greater the injury caused by free acid.

C. EXCESS OF NITRATE OF SILVER IN CONTACT WITH THE PARTICLES OF IODIDE OF SILVER.

When the sensitive plate is lifted out of the bath, the Iodide of Silver is of course in contact with excess of Nitrate of Silver. The presence of this Nitrate is not *essential* during the exposure to light, since, if it be carefully removed by washing in distilled water, the image may still be impressed. In that case however the action is very much slower than before,—twice, or perhaps three times the usual exposure being required,—so that the Nitrate may be said to produce an *accelerating* effect.

This accelerating influence however is not in proportion to the *quantity* of the soluble Nitrate present; what is required is merely that there should be *a decided excess*, and when that is established nothing is gained by increasing it.

It appears that some of the soluble Salts of Silver accelerate more strongly than others, and this is precisely what we should have anticipated upon theoretical grounds.

In the Nitrate of Silver, it is *the base* and not *the acid* of the salt which is required. Supposing the acid to exert

an influence, it would be in the opposite direction; and hence an *Oxide of Silver* in the film accelerates much more powerfully than *a Nitrate* of the Oxide—or the Nitrate of Silver, as we term it.

In this way, it is conceived that the excessive sensitiveness obtained by using strongly fused Nitrate of Silver may be explained; in that state it contains Oxide of Silver, and yields an alkaline bath. Besides oxide, *Nitrite* of Silver is also present; but this salt does not accelerate to an equal extent with the former.

D. THE PROPORTION OF IODIDE OF SILVER CONTAINED IN THE FILM.

Other circumstances being equal, there is a difference in sensitiveness between various films depending upon *the amount of Iodide of Silver* which they contain; although not great, yet it is sufficiently distinct to be worthy of notice.

By the performance of careful experiments many times repeated, it was found that, provided the Nitrate Bath was neutral, *the pale opalescent films* received the impression of a feeble ray of light somewhat more readily than the dense and creamy films.

That such would be the case might have been anticipated. The more dilute the solution from which Chloride or Iodide of Silver is precipitated, the more gradual the precipitation, and the more finely divided will the particles of the precipitate be. Hence it is easy to understand that they would be more sensitive to the influence of light. The difference in the two cases however being but slight, is alluded to simply to remove an impression which would otherwise most probably occur to the mind of the reader, that the most rapid effects would be obtained by *increasing* the amount of Iodide.

Practically speaking, this idea would lead to wrong con-

clusions. A dense film of Iodide, as will be shown by-and-by in the following Sections, gives a more marked image in a case where the light is very intense and the exposure prolonged; but ordinarily speaking, a comparatively transparent film produces a picture equally well with the other, if the presence of acids—which have been shown to be especially injurious to weak films—is excluded.

E. ADDITION TO THE FILM OF BODIES IN A STATE OF CHANGE AND TENDING TO ABSORB OXYGEN.

The effect of adding substances to the film which possess a very strong attraction for oxygen, such as Gallic and Pyrogallic Acids, is to augment the effect produced by the actinic rays in a very marked degree. The action however is too violent under such circumstances, and cannot be restrained within proper limits; so that the hopes which were at one time entertained of combining the development and the impression of the image in one operation, and so producing a picture visible on removal from the Camera, do not appear at present likely to meet with their fulfilment.*

There are however certain chemical agents which may be employed as "accelerators," the characteristic property of which is, that they possess a certain amount of attraction for oxygen, although not sufficient to entitle them to rank amongst the list of "developers."

The principal of these are as follows:—Iodide of Iron, Nitrous Acid and its salts, Grape Sugar, and the various essential oils, as Oil of Cloves, etc.

Iodide of Iron added to Collodion is represented in the film by Protonitrate of Iron thus:—

* The association of Gallic Acid with the Iodide of Silver is employed in the Calotype process in order to increase the sensibility, a portion of Acetic Acid being added at the same time, to preserve the clearness of the whites under the influence of the developer.

Iodide of Iron + Nitrate of Silver
= Iodide of Silver + Nitrate of Iron.

The quantity of Protonitrate formed is exceedingly small; otherwise probably in a neutral film the same universal decomposition as that following the use of Gallic and Pyrogallic Acids would result.

The accelerating powers of the Nitrites were pointed out by the Abbé Laborde and by Mr. Hadow in papers published shortly since, and as nearly as possible at the same time.

An important remark on the use of accelerators, and one worthy of note, is this,—that their effects are by far the most marked when the film is not in a neutral condition; in other words, that a great part of their operation consists in *counteracting the retarding effect of free Nitric Acid.*

The Author found that the addition of Iodide of Iron in moderate proportion, increased the sensitiveness of an opalescent neutral film by no more than *one-sixth* of the total exposure; a comparatively insignificant effect to what is commonly noticed. In the case of the Essential Oils no difference at all could be observed; and yet it has been shown that they accelerate strongly when brown Collodion and an acid Bath are employed.

F. DEPRESSION OF TEMPERATURE AND OTHER CAUSES NOT YET THOROUGHLY EXPLAINED.

A few words will suffice for this head. The influence of temperature upon Photographic processes is seen most evidently perhaps during the development of the latent image, and therefore it will be alluded to again in the next Section; but independent of this, there is reason to think that the *sensitiveness of the plate to light* is interfered with more or less by a reduction of atmospheric temperature below a certain point. To obviate it many practical ope-

rators advise to stand the bottle containing the Nitrate Bath in warm water for a short time if the mercurial thermometer sinks below 40 degrees.

Various retarding causes, the nature of which has not yet been explained.—The most experienced Photographers occasionally complain that a particular sample of Collodion, prepared in the usual way, and with all the proper precautions, has disappointed their expectations. Without possessing any obvious external peculiarity, it proves to be highly insensitive to light and gives a faint image wanting in intensity. The Author has never himself met with anything of the kind, and he attributes his exemption to the fact of *the Ether* employed by him having always been previously rectified from caustic Alkali. It is probable that some impurities may occasionally find their way into commercial Ether, and that the insensitiveness is so explained. Nevertheless this cause of failure is under any circumstances a very rare one, and especially so if common pains be taken in selecting the sample of Ether. The amateur need not be discouraged by the mention of it, from prosecuting his experiments with vigour.

SECTION II.

Conditions which affect the development of the latent Image.

The general theory of the development of a latent image by means of a reducing agent having been already given, the subject will now be entered into more fully as far as regards its application to the Collodio-Iodide of Silver. In the remarks about to be made, it is intended to speak of the development, disconnected as far as possible from the action of the light, leaving until afterwards the discussion of those phenomena in which both processes are more immediately concerned.

The following circumstances will be treated of in order,

as influencing the development of the image.—A. The presence of free Nitrate of Silver upon the surface of the film.—B. The activity of the developing agent.—C. The presence of free acid.—D. Of easily reducible salts, or of oxide of Silver in the film.—E. The temperature of the solutions employed to develope.

A. PRESENCE OF FREE NITRATE OF SILVER ON THE SURFACE OF THE FILM DURING THE REDUCING PROCESS.

This, as being the most important of all, is placed first, and it is intended to lay great stress upon it. We have already seen, that as far as the action of light is concerned, free Nitrate of Silver is not actually required, and that a film of Collodio-Iodide of Silver is capable of receiving the radiant impression in the Camera, even if it have been previously washed with care. It is not however immediately seen that such is the case, since on removing the plate to the dark room and covering it with a reducing agent, no image is brought out. If however it be dipped for an instant in the Bath, in order to restore the Nitrate of Silver which had been washed away, then the picture developes very well. Therefore the soluble Silver Salt, useful before only as an accelerator, is in the development essentially required.

The same thing is shown more completely by further experiments. The ultimate intensity of the image is regulated entirely by the supply of Nitrate of Silver; if too little of that salt is added, then the image is feeble or altogether imperfect in parts; if, on the other hand, too much is used, and the action continued, perfect opacity and destruction of half tones is the result.

These facts refer to the presence of Nitrate of Silver upon the film during the development, independently of the manner in which it was added, whether by the use of

a strong Bath or by subsequent addition to the developing solution.

B. STRENGTH OF THE DEVELOPING AGENT.

No increase of power in the developer will suffice to bring out an image either when insufficiently impressed by Light, or when the proportion of Nitrate of Silver is too small. The advantage gained by the use of a strong developing agent may be said to be principally *in point of time*. A weak developer takes a longer time to act, but produces the same effect in the end. Gallic Acid is not usually employed to develope Collodion pictures, because it reduces so slowly that there is a danger of pouring it off before the action is completed, and in that case the half tones of the picture would be deficient. Pyrogallic Acid, Protosulphate and Protonitrate of Iron act more quickly, but there is a marked difference between the three in this respect. As far as relates to the number of grains required to produce a given effect, Pyrogallic Acid is at least four times as strong as the crystallized Protosulphate of Iron, and twenty times more so than the Protonitrate of Iron. The comparative feebleness of the Protonitrate of Iron is probably attributable to the oxidizing nature of the acid it contains. It is the *protoxide* of Iron, or base of the salt, which acts as the reducing agent, and the association of an acid like the Nitric with this base impedes the effect. It will be seen, as we proceed, that the employment of the Protonitrate of Iron has reference to a peculiar modification in the *colour* of the image produced by the Nitric Acid in the salt.

Pyrogallic *Acid*, so called, being a strictly neutral substance, is in that respect favourably constituted for a reducing agent; indeed in practice it is found to be too violent in action, and to produce universal decomposition, unless a portion of weak acid like Acetic is added to it.

C. FREE ACID IN THE FILM DURING REDUCTION.

All acids tend to retard the reduction of the image; as well as to increase the length of the exposure to light. Nitric Acid especially does so, doubtless from the powerful oxidizing properties it possesses. Acetic Acid acts much more feebly in this respect, and indeed it is usual to add a portion of Acetic Acid to Sulphate of Iron to enable it to flow more readily over the plate and to develope more evenly. Also, as has been shown, the Pyrogallic Acid does not admit of being used without Acetic or some other acid to moderate its violence.

The evils of Nitric Acid in the developing process are especially seen when the proportion of Iodide of Silver in the film, and also of excess of Nitrate of Silver, is small; in that case the deposition of metallic silver is oftentimes altogether prevented in parts of the plate.

It will be seen, as we proceed, that Nitric Acid, added to the developer, possesses a property of brightening the surface of the reduced metal. It is therefore often used by Photographers, but always with caution, from the facts above stated.

If we compare together the retarding effects of free acid upon the action of Light and upon the development, we see that the former is by far the most marked—that is to say, that a small quantity of acid produces a more decided influence upon the impression of the image in the Camera than it does upon the bringing out of that image by means of a reducing agent.

D. PRESENCE OF NITRITE OR OF OXIDE OF SILVER IN THE FILM.

Both Nitrite of Silver and Oxide of Silver are present in Nitrate of Silver which has been very strongly fused.

Hence, if the fused Nitrate is employed for making a Bath, these substances find their way into the film.

It was shown in the last Section that Nitrite and Oxide of Silver both act as accelerators to the luminous agency; but independently of this, they produce a curious change also in the process of development.

The image comes out almost instantaneously and with great force, so that the operator is inclined to think that he has mistaken the proportions, and that his developer is too strong.

It is stated by the Abbé Laborde, that when the Bath contains Nitrites, even Gallic Acid, a comparatively feeble agent, will suffice to bring out the image very rapidly.*

The cause of these peculiarities is easily explained. As strong acids are opposed to reduction, so of course their removal, or their substitution by others of a weaker nature, facilitates reduction. Thus *acid* Nitrate of Silver is more difficult to reduce than *neutral* Nitrate,—Nitrate of Silver more so than *Nitrite*,—and Nitrite more so than the *Oxide* of Silver.

E. TEMPERATURE OF THE SOLUTIONS.

All that is important on this head may be said in few words.

Reduction of the oxides of noble metals always proceeds more rapidly in proportion as the temperature rises. Photographers avail themselves occasionally of a knowledge of this fact by slightly warming the solutions if the mercurial thermometer is found to fall below a certain point.

It may happen sometimes, when the heat of the atmosphere is excessive, that a developer of the usual strength

* The reader is referred to Part III. for an explanation of the Chemistry of the Nitrites. Nitrous Acid, which is the acid of those salts, contrasts strongly in its properties with Nitric Acid. It is a very feebly acid substance, even more so than Acetic Acid.

is found to be too violent in action; in this case it will be necessary to reduce the proportions slightly.

SECTION III.

Hypotheses on the nature of the change produced on Iodide of Silver by the action of Light.

The student will remember that it has already been laid down in Section I., that the change produced, whatever be its nature, is a *positive change*, and not the mere commencement of a reducing process afterwards to be completed by other means.

The effect of *over*-exposing a plate to the luminous image of the Camera, is not to increase the facility of the subsequent developing process, but to break up and destroy the integrity of the image. The "high lights" act violently at first, until apparently the Iodide of Silver on which they fall is not easily susceptible of further change, and then remain quiescent. The half shadows, on the other hand, progress steadily, so that eventually they overtake the others; the consequence of this is, that on developing, no picture at all makes its appearance, or at least a very ill-defined one, and the whole plate is covered with a veil of metallic silver.

A *maximum of effect* then is always attained after a time; but still *the degree* of this maximum varies much in different cases. The rule is, that the more powerful the light and the longer it is intended it should act, the greater must be the quantity of Iodide in the film. A transparent film receives the impression of a feeble ray as speedily, and perhaps more so, than a creamy film, and it gives under those circumstances an equal amount of intensity on the application of the developer. But if the light is unusually strong—such, for instance, as the diffused light of the sky—then in that case the intensity is greatest with the more dense film.

All this seems to show that a *molecular change* of some kind is set up which proceeds to a greater or less extent *in proportion to the number of the particles.*

What then, it may be asked, is this molecular change? Clearly it is not of such a nature as to alter, to any material degree, either the composition or the properties of the salt. No Iodine leaves the surface!—if so, there would be a difference in the appearance of the film, or in its solubility in Hyposulphite of Soda.

The following diagrams may perhaps be useful in assisting to form a notion of what is meant by a "molecular change."

Fig. 1. Fig. 2.

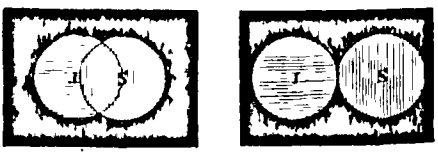


Fig. 1 represents a compound molecule of Iodide of Silver, the component atoms of which are associated closely together.

Fig. 2. The same after the action of a disturbing force. The simple molecules have not altogether separated from each other, but they are prepared to do so, touching only at a single point.

Now the effect produced on such a combination by a developer is understood, if we suppose that in the first case the affinity of the Iodine for Silver is too great to allow of its separation; but in the second, this affinity having been loosened, the structure gives way, and metallic silver is the result.

This hypothesis has at all events the merit of simplicity, but we have no security whatever that it is really the correct explanation. The fact of no development being at-

tainable without the presence of free Nitrate of Silver, renders it exceedingly difficult for us to trace out the exact source of the metallic deposit. (See page 46.)

Second Hypothesis, that the Iodide of Silver does not suffer reduction, but that the image is formed from the soluble Nitrate of Silver.—In this case, as the last, a molecular change is supposed, but not of such a nature as to cause the ultimate separation of the Iodine and Silver under the influence of the developer. The relation of the component particles of the Iodide of Silver towards each other is modified in such a way, that *the reduction of the Nitrate in contact with those particles* is facilitated, and the deposit of metal so formed *is caused to adhere.**

Lest it should be thought that the idea of the particles of reduced silver "being caused to adhere to the plate by a molecular change on the surface where they were deposited," is strange and far-fetched, the reader is invited to give his attention to the following statement of facts.—

If, during the process of the ordinary development of a Collodion Photograph, the action be stopped as soon as the picture has fully appeared, and the plate be then washed and treated with Cyanide of Potassium, or Hyposulphite of Soda, until the whole of the Iodide of Silver has been removed,—an image will be obtained which is perfect in every part, but *very pale by transmitted light*. This pale image is then to be taken back again into the dark room and treated with a fresh dose of Pyrogallic Acid, to which *Nitrate of Silver* has been added. Immediately it becomes

* This view of the production of the Photographic image was originally suggested to the Author by Mr. E. A. Hadow. It is well illustrated by the fact familiar to Chemists, that a saturated solution of any salt about to crystallize, when poured over a glass plate, deposits the crystals first on the excited lines previously formed by rubbing with a dry cloth, or by subsequent stirring with a glass rod. (*Vide* 'Photographic Journal,' vol. ii. p. 71, for an interesting communication by Mr. Ross, Architect, of New York.)

very much blacker, and continues to do so even to complete opacity if the supply of Nitrate be kept up.

Here then is direct proof of a deposit formed from the Nitrate, and not from the Iodide of Silver, since the whole of that substance had been previously removed; but the peculiarity most worthy of notice is this—*that the deposit forms only upon the image, and not at all upon the other parts of the plate.* Even if the Iodide, untouched by light, be allowed to remain, the same rule holds good;—the Pyrogallic Acid and Nitrate of Silver react upon each other and produce a metallic deposit, but this deposit seems to have no affinity for the unaltered Iodide on the part of the plate corresponding to the shadows, but settles down in preference on the Iodide already blackened by the developer.

Now in instituting a comparison between the respective merits of these two hypotheses, we are brought at last to the conclusion that it is really a matter of small consequence which is preferred. One point however is of importance, and it is necessary that we should bear it in mind, viz. that under either supposition there can be no doubt but that *by far the greater portion* of every Photographic image, of any intensity, is certainly derived from a decomposition of the Nitrate and not from the Iodide of Silver. If the student should attempt to increase the intensity of the Photograph by adding to the quantity of the Iodide, he will in general be working in the wrong direction; whereas by viewing the Iodide in the light, as it were, of a *foundation surface* on which the metallic particles derived from the Nitrate are to be laid down in regular order,—the thickness of the image being formed by the *superposition* of such particles,—he will, however he stand with regard to theory, be correct as far as practical considerations are concerned.

A close observation of facts cannot fail to lead us even-

tually to the conclusion that the action of light upon Iodide of Silver is in all cases a *surface action*, and that the image is entirely superficial and not at all in the substance of the film. Indeed, by operating in a particular manner, such can actually be demonstrated to be the case, since, after fixing with the Cyanide, the image may be wiped away with a pledget of cotton-wool, leaving the film below perfectly intact.

SECTION IV.

On the most probable causes of the superior sensitiveness of the Collodio-Iodide of Silver.

The present Chapter would be incomplete without the introduction of a few remarks upon this subject.

The sensibility of Iodide of Silver upon Collodion is certainly greatly superior to that of the same salt employed in conjunction with any other vehicle at present known. Hence the Collodio-Iodide film will certainly supersede the paper processes in all cases where objects liable to move are to be copied.

The causes of this superior sensitiveness may be arranged under two heads—mechanical and chemical.

A. MECHANICAL CAUSES.

1. *The state of loose coagulation* of a Collodion film.—This is peculiarly favourable to the perfect exposure of every particle of the Iodide in a state of the finest division to the action of the light; the component molecules not being strongly imprisoned, the play of chemical affinities is thereby promoted.

2. *Its employment in a moist state.*—It was noticed in an early part of the work, that all Salts of Silver were more sensitive to light when moist than they would have been if previously dried. A Collodion film may be washed

and dried without its properties being actually destroyed, but by such a course of procedure most of the advantages attending its employment are lost.

B. CHEMICAL CAUSES.

It is not probable that any chemical decomposition of the Pyroxyline takes place during the exposure to light. On the contrary, there is reason to think that the peculiar photographic properties of this substance depend entirely upon mechanical conditions. There are however certain causes which increase the sensitiveness of a Collodion film, which are strictly *chemical* in their nature.

1. *The comparatively neutral condition in which such films are employed.*—In the various paper processes it is usual to add much Acetic Acid in sensitizing the paper, in order to promote clearness of the image, and this of course diminishes the sensibility to light.

2. *The influence of the organic matters present.*—Both Alcohol and Ether are bodies possessing a tendency to the absorption of oxygen, and hence they may be supposed to act in some degree as accelerators to the luminous agency.

Estimate of the amount of Sensitiveness ordinarily attainable with the Collodio-Iodide of Silver.—The film of Iodide of Silver upon Collodion, although affording us the most sensitive photographic surface at present known, or rather the most sensitive which has been *perfected* and made available for common use, can yet scarcely be said to be *instantaneous* in its impressibility by the luminous image of the Camera. An exposure of a fraction of a second for distant objects brightly illuminated, and a single second for portraits and objects close at hand, is the utmost degree of sensitiveness which the Author has been able to obtain, consistently with a regard to "gradation of tone" in the image; and he has invariably found that if by the

use of powerful accelerators the sensitiveness were increased much beyond this point, that the representation of the lighter parts of the object was unduly magnified.

SECTION V.

On the Gradation of Tone in the finished Photograph, and the circumstances affecting it.

All persons who are in the habit of examining the productions of the Photographic Art, are well aware that there is oftentimes to be seen in them a tendency to exaggeration in the lighter parts of the picture, and a heavy, unnatural darkness about the shadows. Now no doubt much of this depends upon the fact already stated, that the chemical rays of light abound in blue and in white colours, and are, comparatively speaking, deficient in those of a darker and more sombre hue. But independently of this, the *nature of the sensitive surface* employed has much to do with the result, and it is not altogether *the Light* which is in fault in such cases. A Photographer who is desirous of attaining to anything like excellence in the practice of his art, must study this subject carefully, and learn not only to develope the picture well, but also how *to prepare the surface of Iodide of Silver in the most efficient state for being impressed by the chemical radiations.*

Now Iodide of Silver, although in all cases the same substance chemically speaking, admits of much variety in the ease and rapidity with which its component molecules are disturbed. Not only is one film more *sensitive* than another, which would be a point of comparatively small importance, but there is also a great difference *in the gradation of tone* of the resulting image, and this, too, independent of the process of development, and supposing it to have been conducted with care.

The best kind of sensitive surface is the one on the molecular structure of which every chemical ray produces a definite effect and in proportion to its intensity.

On the other hand, that film is to be avoided where the change produced by the actinic rays is slow in commencing, but proceeds afterwards in a tumultuous and irregular manner.

In treating the subject, the following points will be brought forward.—A. The condition of film best adapted to produce gradation of tone under strictly neutral conditions.—B. Modifications produced by the addition of acid. —C. By the use of accelerating agents.

A. STRUCTURE OF FILM BEST UNDER NEUTRAL CONDITIONS.

The Author has made experiments on this subject with considerable care.

The plan pursued was to arrange together a number of objects, contrasting as strongly as possible in their powers of reflecting light, and to test the films upon the combination. Perhaps however nothing can be better in this respect than a portrait from the life, and especially one in which the drapery includes both black and white.

In order further to ensure the accuracy of the result, it is necessary that the Nitrate Bath should consist of *pure Nitrate* of Silver, free from Nitrite, and that the Collodion should be colourless or nearly so.

By comparing various films of Iodide of Silver of different thickness, it was found that the smaller the proportion of Iodide they contained, down to a certain point, the better the result.

The exact effect of diminishing the number of particles seemed to be, to assist the action of the feeble rays somewhat, but in an especial manner *to curb the violence of the more extreme rays;* hence a better correspondence between them was established, and the image was perfect in every

part without being "overdone" in the high lights. In consequence of this, the pictures were more stereoscopic, —appearing as it were to stand out from the glass.

In the case of the dense and creamy films, the same result could not be attained; either the lights were good and the shadows unnaturally dark, or if the exposure was prolonged, then the shadows came out well, but the lights were lost.

The creamy films therefore are not considered to be adapted to yield the finest effects *when employed in a neutral state.*

B. ALTERATION PRODUCED BY THE PRESENCE IN THE FILM OF BODIES ACTING AS RETARDING AGENTS.

Having ascertained the particular structure of film which appeared to answer best under neutral conditions, it was important to examine whether the same rules would apply in cases where an acid of any kind was present.

To preserve a solution of Nitrate of Silver intended for use as a Bath in a chemically neutral condition is always a more or less troublesome task. The free Iodine contained in the Collodion liberates acid in minute quantity at every dip of the plate, and thus tends to reproduce the condition which it had been our object previously to remove. It is therefore more practically useful to determine the best structure of sensitive film adapted for a faintly acid Bath.

The acid which exercises so powerful a retarding influence upon the action of the actinic rays is *the Nitric Acid.* Acetic Acid is far less injurious even when present in larger quantity.

The experiments therefore alluded to in the last division were repeated with a Bath containing a few drops of Nitric Acid, and the result proved that the presence of acid produced a material change.

The transparent films were much injured. The shading was very imperfect, nothing being seen but the highest lights, and those only in patches. In the case of a portrait, the dark portions of the drapery ceased to produce any impression upon the film, the part of the image corresponding to them being represented by the transparent glass without any deposit of metallic silver whatever.*

The opaque and creamy films, on the other hand, seemed but little affected by the acid: the sensitiveness was diminished, but by a longer exposure a good picture could be obtained.

On repeating experiments like these many times, the conclusion arrived at was as follows,—viz. that in order to ensure gradation of tone the physical structure of the Iodide film should be adapted to the nature and to the amount of the acid which existed in the Bath. If Acetic Acid, and in moderate quantity, a tolerable transparent film succeeded better than an opaque film. If Nitric Acid, then the amount of Iodide to be increased in proportion to the quantity of this acid present.

The gradation of tone probably affected by other retarding agents, not possessing the character of Acids.—The above experiments on the qualities of different films for yielding gradation of tone were conducted under circumstances the most favourable which can be conceived for sensitiveness to actinic influence—the temperature of the atmosphere tolerably high—the time of year, viz. the spring months, the best adapted for rapid impression—the Collodion very pure and with much Alcohol—the Bath chemically neutral. Under these circumstances it may be conceived that

* The strength of the Nitrate Bath, as representing the proportion of free Nitrate of Silver upon the surface of the image during the process of development, also affects the result when free Nitric Acid is added. By increasing the amount of soluble Silver Salt, we succeed oftentimes in bringing out the half-tones of the image under very unfavourable conditions. This fact has already been alluded to in the second Section.

the mobility, so to speak, of the particles was at its maximum, and in consequence it was found almost impossible to reduce the amount of Iodide too far. Even when the structure of the film became so slight that scarcely anything could be seen upon the glass, the most vigorous impressions were produced. In this state the sensitive layer might be said to rival the Daguerreotype for slightness and delicacy.

It is very possible however—and on this subject further experiments are required—that if even with a neutral Bath the film had been constructed in such a way as to be less easily impressed by light,—that is to say, if it had contained a much larger proportion of Ether, or if any impurity of a retarding nature had been present in the Collodion,—under those circumstances the same reduction of Iodide would not have been admissible. In other words, as the transparent films were more injured by free acid than the opaque films, so would they also be by other retarding causes independent of acidity.

If this view of the subject be correct, then it will be well to take these causes into account, and to regulate the condition of film by the proportion of Alcohol in the Collodion,—by the temperature of the atmosphere, etc.

Practically speaking however, the presence of acid in the Bath and of Iodine in the Collodion are of the most importance, and especially so, if no means of converting Nitric Acid into Acetic—such as the addition of Acetate of Silver to the Bath, presently to be recommended—have been taken.

C. MODIFICATION OF EFFECT RESULTING FROM USE OF "ACCELERATORS."

By comparing the effects produced by *acids* with those which result from the use of "accelerators," it is soon seen that these two agents are exactly opposite to each other in

their nature. Acids retard the action of Light, accelerators assist it. Acids impede *development*, accelerators hasten it. And so in the case before us we may say—that as acids diminish the "polarity" induced in the particles of Iodide of Silver by Light, so, on the other hand, that accelerators *heighten* it.

It is important to be noticed, as far as the use of these substances is concerned, that although they produce a picture in a shorter time than before, the gradation of tone in such a picture is often inferior. The exaggeration of the light parts, which we are so anxious to avoid, is present usually in a marked degree. If such is not the case, probably the accelerating agent was employed in conjunction with a weak film of Iodide, or much acid was present, the effect of the accelerator being, in that case, expended upon the acid alone.

RECAPITULATION OF FACTS STATED IN THIS SECTION.

That uniformity of action, as far as possible, between feeble and energetic rays of light, is necessary to produce a perfect Photograph, and that this uniformity is promoted by all causes which help forward the former, and restrain the latter.

That a diminution in the proportion of Iodide of Silver in the film is an effectual means of restraining the violence of the extreme rays; but that the extent to which this can safely be carried, without producing absolute insensibility to half-tones, varies with the retarding influences which are at work.

Lastly, that rapidity of impression being of small consequence as compared with perfection of image, accelerating agents should be employed with caution, and their effects carefully watched.

SECTION VI.

On the Fogging of Collodion Plates.

The characteristics of the proper development of a latent image, as already laid down in more places than one, are these:—that the action of the reducing agent should cause a blackening of those parts which had been exposed to light, but produce no effect whatever upon others which had been shielded from it.

It is impossible however to make many experiments in Photography without becoming aware of the fact, that there is a constant liability to failure in this respect; that oftentimes the plate begins, shortly after the application of the developer, to change in colour to a greater or less extent over its whole surface.

This state of things is generally termed "fogging," because the metallic silver having a grey appearance by reflected light, the picture seems, on looking down upon it, as if it were veiled behind a dense fog.

There are two main causes which produce fogging, and they are of a totally distinct kind:—the first is due to irregularity in the action of the light;—the second to impurity in the chemicals employed.

First, to irregularity in the action of the Light.—The luminous image of the Camera is *circumscribed*—some parts are in shadow whilst others are illuminated; if any defect however exist in the construction of the instrument, then a portion of *diffused* light gains entrance. Diffused white light necessarily produces fogging by affecting the Iodide more or less universally. There are many ways besides the one mentioned, in which diffused light may gain entrance into the Camera, but these will be alluded to in the second division of the Work.

Even supposing that the absence of all diffused light is secured, yet fogging may still be produced by simply

exposing the plate to the influence of light for too long a time. In that case, when the developer is poured on, a faint image first appears, and then immediately afterwards a general decomposition. This is caused by the action of the light having ceased to be circumscribed, and the particles of Iodide having become modified in every part of the plate.

Secondly, to impurity of the Chemicals.—When the solutions employed to form the film of Collodio-Iodide are in fault, a universal fogging often takes place on the application of the developer, without the plate having been previously exposed to light. The following are some of the causes of this kind which produce fogging:—

A. *The use of Pyrogallic Acid alone without Acetic Acid.*

B. *The presence of Oxide of Silver in the film, or of oxide associated with weak acids.* (See Section II. of this Chapter.)—In this case the fogging is not so marked as in the last, but still sufficient to spoil the appearance of the picture. A Nitrate Bath can be employed perfectly neutral if it is *pure*;—in other words, it is not the *Nitrate* of Silver which causes fogging, but the Nitrate contaminated with Oxide, Nitrite, or Acetate of Silver.

C. *Presence of organic matter of certain kinds.*—It is probable that substances are formed occasionally as a result of the slow decomposition of the Nitrate Bath, which render it impossible to use the solution in an accurately neutral state. Reference is particularly made at this time to a volatile organic liquid of peculiar smell and neutral reaction, obtained by the Author on distilling an old Nitrate Bath which had probably been exposed to light. This liquid caused fogging to a considerable degree when added to a solution of pure Nitrate of Silver, previously free from this peculiarity.

Remedies for Fogging.—Whatever tends to diminish

the sensitiveness of the plate, also lessens the tendency to fogging. The rule is, that those films, the molecular structure of which is easiest disturbed, are the most liable to be affected by causes producing fogging. Hence the opalescent films employed neutral require an amount of care which would not be necessary in the case of more dense films slightly acid.

The remedies for fogging vary of course with the causes which produced it. The first is to secure the absence of all diffused white light; the second, to purify the chemicals afresh, or to lessen the sensitiveness of the plates by addition of free acid in small quantity.

The addition of acid is a sovereign and most potent remedy for fogging, and when there are not other circumstances which forbid its use, it is the simplest and best to adopt. A weak acid, such as *Acetic*, will in general be found sufficient.

Ultimate causes of Fogging.—It may be desirable to say a few words as to the manner in which *impurity of the chemicals* may probably act in producing fogging. There is no reason to suppose that it causes the Iodide of Silver to be reduced in that part, but simply alters the state of things in such a way that the deposit of metallic silver formed as the result of the action of the developer upon the Nitrate, *adheres not only to the Iodide changed by Light, but also to the unchanged Iodide in a certain measure.* Fogging, when it depends upon the chemicals, is always slight, and the deposit can usually be wiped away with facility. On the other hand, that caused by diffused light is more marked, and adheres with greater firmness.

CHAPTER IX.

ON "POSITIVE" AND "NEGATIVE" COLLODION PHOTOGRAPHS.

THE terms "Positive" and "Negative" occur so frequently in all works and conversations upon the subject of Photography, that it will be impossible for the student to make any progress without thoroughly understanding their meaning.

In attempting to give a clear and simple explanation, the words will be taken in their usual sense, without reference to peculiar varieties of Photographs; such as "transparencies" for the Stereoscope or Magic Lantern, etc.

A Positive may be defined to be a Photograph which gives a natural representation of an object, as it appears to the eye.

A Negative Photograph, on the other hand, is one which has the lights and shadows reversed, so that the appearance of the object is changed or negatived.

Now, the first question obviously suggesting itself on reading this definition for the first time would be,—as to wherein the advantage consisted, of thus misrepresenting objects by a *Negative* Photograph. To this, reply is made as follows:—

That in Photographs taken upon a layer of *Chloride of Silver*, either in the Camera or by superposition, the effect

must necessarily be Negative; the Chloride being *darkened* by *luminous rays*, of course the lights are represented by shadows.

The following simple diagrams will make this obvious:—

Fig. 1. Fig. 2. Fig. 3.

Fig. 1 is an opaque image drawn upon a transparent ground; fig. 2 represents the effect that would be produced by placing it in contact with a layer of sensitive Chloride and exposing to light; and fig. 3 is the result of copying this negative again on Chloride of Silver.

Fig. 3 therefore is a Positive copy of Fig. 1, obtained by means of a negative. By the first operation the tints are reversed; by the second, being reversed again, they are made to correspond to the original.

In this way Negatives are useful;—they enable us to obtain, by a process somewhat analogous to printing, Positive copies, indefinite in number, and all precisely similar in appearance. This capability of multiplying impressions is of the utmost importance, and it has rendered the production of good Negative Photographs of greater consequence than any other branch of the Art.

The character of a Photograph influenced by the manner in which it is viewed.—The same Photograph may often be made to show either as a Positive or as a Negative indifferently. For instance,—supposing a piece of silver leaf to be cut into the shape of a cross and pasted on a square of glass, the appearance presented by it would depend entirely upon the manner in which it was viewed.—

Fig. 1. Fig. 2.

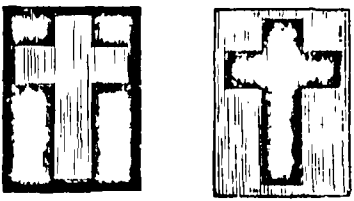


Fig. 1 represents it placed on a layer of black velvet; fig. 2 as held up to the light. If we term it *Positive* in the first case, *id est*, by reflected light, then it is Negative in the second, that is, by transmitted light. The explanation is obvious.

Therefore, if we wish to carry our original definition of Positives and Negatives a little further, we may say, that the former are usually viewed by reflected, and the latter by transmitted, light.

All Photographs however cannot be made to represent both Positives and Negatives. In order to possess this capability, it is necessary that a part of the image should be *transparent*, and the other *opaque but with a bright surface.* These conditions are fulfilled when the Collodio-Iodide of Silver is employed in conjunction with a developing agent.

Every Collodion picture is to a certain extent both Negative and Positive, and it will simplify matters to take this view of the subject. The question is often put by a beginner, How do you obtain the Negatives? To which the natural reply is,—in the same manner as we obtain Positives, the nature of the two being alike.

Although however the general characters of both varieties of Photographs may be combined in a single proof; yet the *excellences* of both cannot be. A surface which appears perfectly opaque when looked down upon, becomes

somewhat translucent on being held up to the light. Consequently, in order to give the same effect, the deposit of metal in a Negative must be proportionably thicker than in the case of a Positive. If it is not so, all the minor details of the image will be invisible,—they do not obstruct the light sufficiently, and hence are not seen.

With these preliminary remarks, we are prepared to investigate more closely the *rationale* of the processes for obtaining Collodion Positives and Negatives. All that refers to paper Positives upon Chloride of Silver will be treated of in a subsequent chapter.

SECTION I.

On Collodion Positives.

Collodion Positives are sometimes termed "direct," because they are obtained by a single operation. The Chloride of Silver, *acted upon by light alone*, is not adapted to yield direct Positives, the reduced surface being dark and therefore incapable of representing the *lights* of a picture. Hence a developing agent is necessarily employed, and the Iodide of Silver substituted for the Chloride, for reasons already given. Collodion Positives are closely allied in their nature to *Daguerreotypes*. The difference between the two consists principally in the surface used to sustain the sensitive layer, and the nature of the substance by which the invisible image is developed.

In a Collodion Positive the lights are formed by the bright surface of the reduced metal, and the shadows by a black background showing through the transparent portions of the plate.

Two main points are to be attended to in the production of these Photographs.

First, to obtain an image distinct in every part, *but of comparatively small intensity*.—If the deposit of reduced

metal is too thick, the dark background is not seen to a sufficient extent, and the picture is in consequence deficient in shadow.

Secondly, to *whiten* the surface of the reduced metal as much as possible, in order to produce a sufficient contrast to the dark background. Iodide of Silver developed in the usual way presents a dull yellow appearance which is sombre and unpleasing.

The theory of this subject may be fully treated of under the following heads.—A. The time of exposure to light.—B. The structure of film best adapted for the purpose.—C. Modification of the developer in order to brighten the tint.—D. Peculiarities of Pyrogallic Acid and the Proto-salts of Iron employed to develope Collodion Positives.—F. The purity of the tint affected by Nitrite and Oxide of Silver in the film.—F. Processes for whitening glass Positives by a subsequent chemical action independent of the development.

A. THE TIME OF EXPOSURE TO LIGHT REQUIRED FOR COLLODION POSITIVES.

The rule to be followed is—to expose the plate for such a length of time that, after developing, *the darkest shadows are distinctly seen by reflected light.* If the film is in good condition (and the plate has not been over-developed) the highest lights will be scarcely, or not at all, overdone by the time that this takes place; but if, on the other hand, the film is not adapted for taking Positives, then the operator must be content to sacrifice the shadows to a certain extent, and to regulate the exposure by the appearance of the lights. In that way perhaps a tolerable picture may be obtained, although somewhat sombre in the dark parts.

The exposure required for a Collodion Positive is never more than *half* as much as that necessary for obtaining a negative with the same film.

B. THE STRUCTURE OF FILM BEST ADAPTED FOR COLLODION POSITIVES.

This subject has already been treated of in the fifth Section of the preceding chapter. By keeping in view the nature of our requirements, it is easy to construct a film fitted for taking Collodion Positives.

The principal points to be attended to are two in number, viz.—to restrain the violence of the actinic rays—and to keep the development of the image within proper bounds. The first of these is accomplished by reducing the amount of Iodide of Silver in the film, and the second, by lessening the quantity of free Nitrate of Silver upon its surface, or, in other words, by diminishing the strength of the Bath.

Under these circumstances however, it is necessary that active retarding agents, such as powerful acids, etc., should be excluded. If free acid is present in the film, and it is not thought desirable to remove it, then the amount of Iodide of Silver must be regulated according to the nature of the acid and also to its quantity. The excess of Nitrate of Silver too upon the surface of the film must be greater than if no acid had been present.

C. MODIFICATION OF THE DEVELOPING PROCESS IN ORDER TO BRIGHTEN THE IMAGE.

Although the Photographic image developed by the usual reagents may be said to consist in all cases probably of metallic Silver, yet the appearance presented by it varies much with the nature of the developer. This subject has already been alluded to at page 47, but it will be necessary to examine it a little further.

There are two principal varieties of metallic deposit commonly to be noticed in the reduced silver forming the lights of a Collodion Positive. They differ from each other

in *appearance*,—one possesses metallic lustre, the other does not.

The first is a surface bright and sparkling like frosted silver, very white when produced in perfection, but with occasionally a greyish or tin-foil hue.

The second is of a pure white tint or of a white slightly inclining to yellow or grey; *it has no appearance of a metal*, the colour being *dead* like that of a piece of chalk.

These varieties require exactly opposite conditions of developer to produce them.

The first is obtained by means of a reducing agent, *checked as it were in its action by the presence of a strong acid;* consequently the development is modified, and the particles of Silver are large and crystalline. *The second*, on the other hand, results when the action of the developer is sudden and violent, no impediment being offered by the presence of acid, except in minute quantity;* the particles of metallic Silver are here smaller than before, and being comparatively amorphous they reflect light in a different manner.

D. PECULIARITIES OF PYROGALLIC ACID AND OF THE PROTOSALTS OF IRON, EMPLOYED AS DEVELOPERS FOR COLLODION POSITIVES.

a. *Pyrogallic Acid.*—This substance, when used with Acetic Acid, as is usual for negative pictures, produces a surface which is dull and yellow. Mr. Horne first proposed to obviate this by substituting Nitric Acid *in small*

* The extent to which the colour of the image is affected by the *rapidity of deposition* of its particles is shown by the fact that in any Collodion Photograph the metallic Silver first formed upon the application of the developer, *id est*, that reduced from the Iodide itself, or precipitated immediately in contact with the changed Iodide, is considerably whiter than the subsequent portion obtained by prolonging the development. The latter forms more slowly, and has a dull grey or yellow colour. With care it may sometimes be wiped away, and the *white substratum* exposed to view.

quantity for the Acetic. The surface produced by Pyrogallic with Nitric Acid is lustreless, but very white, if the solution is used of the proper strength. On attempting to increase the amount of Nitric Acid the deposit becomes more metallic, but the half tones of the picture are injured. Pyrogallic Acid, although an active developer, does not allow of the addition of mineral acid to the same extent as the Salts of Iron. It requires, too, a fair proportion of Nitrate of Silver on the film, or the development will be imperfect in parts of the plate.

b. *Sulphate of Iron.*—This salt is a most energetic developer, and often brings out a picture in cases where others would fail. To produce by means of it the tint which has been characterized as a dead white with absence of metallic lustre, it should be used of such a strength that the picture comes out almost instantaneously in all its details. There is no danger, as may at first seem, of injuring the gradation of tone by this apparently violent method of proceeding, *if the proportion of Nitrate of Silver be kept low* and the solution poured off tolerably quickly.

For the bright sparkling surface a considerable addition of acid, and best of all of *Nitric Acid*, will be required. Too much however of this substance must not be used, or the reduction will be irregular. The Nitrate Bath is to be employed somewhat more concentrated than before, in order to compensate for the retarding effect of Nitric Acid upon the development. The pale and transparent films of Iodide of Silver, with small excess of free Nitrate, are not adapted for Positives to be developed in this way. They are injured by the acid, and the development of the image is imperfect.

c. *Protonitrate of Iron.*—This was first employed as a developing agent for Collodion Positives by Dr. Diamond. It is remarkable as giving a surface of brilliant metallic lustre without any addition of free acid. Theoretically

speaking, it may be considered as closely corresponding to the Sulphate of Iron with Nitric Acid. There are however slight practical differences between them, which are perhaps in favour of the Protonitrate.

It was shown in the second Section of the previous Chapter, that the reducing powers of the *Protoxide* of Iron were in inverse ratio to the strength of the acid with which it was associated. Hence the *Nitrate* is by far the most feeble developer of all the Protosalts of Iron.

The rules already given for the use of Sulphate of Iron acidified with Nitric Acid, apply also to the Nitrate of Iron;—the proportion of free Nitrate of Silver upon the film must be *large*, and the Iodide of Silver *not too transparent*.

The greatest objection to the Nitrate of Iron is the difficulty of obtaining it in the solid form; hence it is necessary to prepare it in small portions at a time, as required.

E. THE TINT OF A COLLODION POSITIVE AFFECTED BY THE PRESENCE OF NITRITE AND OXIDE OF SILVER IN THE FILM.

It has been shown in Chapter VIII. that the Nitr*ite* and the Oxide of Silver, as occurring in Nitrate of Silver which has been strongly fused, exercise an important influence upon the impression of the image in the Camera, and also upon its subsequent development by a reducing agent. We notice now certain other effects produced by the presence of these bodies.

If the Nitrate Bath contain even a small portion of Nitrite or of Oxide of Silver, a peculiar and unpleasant tint, which has been sometimes termed "solarization," is seen upon those parts of the plate corresponding to the highest lights. There is reason also to think that the presence of *Acetate* or of any other easily reducible salt of Silver in the film, injures the purity of the white colour in the parts

most acted upon by the light. The Nitrite and the Oxide of Silver however are, practically speaking, the most remarkable in this respect.

Over-exposure of the plate in the Camera also influences the tint to some extent, even when the Bath is pure; if the Light has been allowed to act for too long a time, the deposit is invariably less bright than usual.

F. ON CERTAIN PROCESSES FOR WHITENING THE IMAGE BY THE USE OF CHEMICAL REAGENTS SUBSEQUENT TO THE DEVELOPMENT.

In place of producing a bright deposit by modifying the condition of the reducing agent, it has been proposed to develope the Positive image in the usual way, such as is common for Negatives, and to whiten subsequently by the use of chemical reagents.

Two modes of effecting this will be described. The first is taken from an anonymous communication in the 'Photographic Journal,' vol. i. p. 230; it is as follows:—

The metallic surface is converted entirely into Iodide of Silver by exposing it to the fumes of Iodine at a slightly elevated temperature. It is then exposed to a strong light,—if possible, to the direct rays of the sun,—until it is changed to *a white and amorphous powder.*

This conversion of Iodide of Silver into a white substance, insoluble in solution of Hyposulphite of Soda, has long been familiar to Daguerreotypists, but the exact composition of the powder has not been ascertained. Plainly, Iodine leaves the surface under the powerful influence of the Light, and this in itself is most interesting, theoretically considered.

Second plan, by Bichloride of Mercury.—The whitening process by Bichloride of Mercury was originally introduced by Mr. Archer. The image is first developed in the usual manner, fixed, and washed. It is then treated with

the solution of Bichloride, the effect of which is to produce almost immediately an interesting series of changes in colour. The surface first *darkens considerably*, until it becomes of an ash-grey, approaching to black; it does not however remain at this stage, but in a very few minutes begins to get lighter, and gradually assumes a *pure white* tint, or a white slightly inclining to blue. It is then seen, on examination, that the whole substance of the deposit is entirely converted into this white powder.

The *rationale* of the reaction of Bichloride of Mercury upon metallic silver in a finely divided state appears to be as follows:—The Chlorine contained in the mercurial salt becomes divided between the Mercury and the Silver, a portion of it passing to the latter metal and converting it into a Protochloride: this Protochloride afterwards unites itself with the Protochloride of Mercury resulting from the reduction of the Bichloride, and forms with it a double Chloride of Mercury and Silver, thus:—

$$HgCl_2 + Ag = HgCl\,AgCl.*$$

The white powder therefore is no longer *a metal*, but a compound salt; and the effects produced on treating it with various reagents fully justify this view of its composition.

It is not easy to account for the *preliminary blackening* of the surface on first pouring on the solution, but probably it is caused by the Bichloride giving up *the whole* instead of *a part only* of its Chlorine, and forming either Oxide of Mercury or Amalgam of Mercury and Silver.

It may be useful to remark, that the whitening process by Bichloride of Mercury always produces the effect of lessening the intensity of the image to a slight extent, so that the black background is more readily seen than before. This is accounted for by the fact of the *porous and*

* The writer has not been able to ascertain whether any exact analyses have been made of this salt; but he presumes that the nature of the change must be somewhat as here represented.

spongy texture of the double salt which forms the white powder diminishing the resistance to the passage of rays of light and hence increasing the translucency.

Another point worthy of notice is, that the colour of the whitened surface is not always precisely the same. Occasionally it has a *bluish* tint, which is particularly objectionable. As far as could be gathered from a few experiments made to determine the cause of this, the blueness depended somewhat upon the structure of the Iodide film, being most marked in the transparent varieties.

RECAPITULATION OF MAIN FACTS CONTAINED IN THIS SECTION.

Before passing on to the next Section, we pause for a moment, to condense in a few words what has been said on the subject of the various tints obtainable in Glass Positives.

The artist is to be guided in his selection of a developer by the structure and condition of the film employed. If it is comparatively dense and acid, and yet he wishes to obtain an image free from metallic lustre, it will be advisable to employ either Pyrogallic Acid with minute quantity of Nitric Acid, or to whiten subsequently by the Bichloride of Mercury. Under such circumstances however, it is more easy to develope a sparkling and metallic image by the Sulphate of Iron and Nitric Acid, or by the Nitrate of Iron. If the film, in place of being dense and acid, is translucent and neutral, it is not well adapted for the metallic variety of deposit, nor for the Bichloride of Mercury process, but it will give excellent results with strong solution of Sulphate of Iron free from Nitric Acid, the image being of a dead white and lustreless.

SECTION II.

On Collodion Negatives.

As in the case of a direct Positive we require an image which is *feeble* though distinct, so, on the other hand, for a Negative it is necessary to obtain one of considerable intensity. In the Chapter which immediately follows the present it will be shown that in printing glass Negatives—or in producing from them Positive copies upon Chloride of Silver paper—a good result cannot be secured unless the Negative is sufficiently dark to obstruct light strongly.

The various steps in the process of obtaining Collodion Negatives may be included under the following heads:—A. The exposure to light.—B. The structure of film best adapted for Negatives.—C. The means by which the intensity is increased.—D. The colour of Negatives as influencing their opacity to chemical rays.—E. Peculiarities of Pyrogallic Acid and the Protosalts of Iron employed to develope negatives.—F. The conversion of finished Positives into Negatives.

A. THE EXPOSURE TO LIGHT REQUIRED FOR NEGATIVES.

The same rule may be applied as that already given for Positives, viz. to expose until the feeblest radiations have had time to impress themselves. The number of seconds required for a picture to be viewed as a Negative by transmitted light, will be at least double that taken for a Positive seen by reflected light. The appearance of the *dark shadows* is a better guide to the proper time of exposure than the intensity of the lights. By bearing this fact in mind, the operator will be likely to avoid the error of *under-exposing*, so commonly committed in the case of glass Negatives.

B. THE STRUCTURE OF FILM BEST FITTED FOR NEGATIVES.

The proportion of Iodide of Silver in the film intended for Negatives cannot conveniently be reduced beyond a certain point. Not that the blue transparent films give too little intensity, as sometimes stated—for with a stronger developer and more Nitrate of Silver added, any amount of blackness can be produced with the weakest Iodide film—*but that they do not admit of being exposed in the Camera for the requisite length of time without a certain amount of fogging taking place, under the subsequent influence of the developer.* This subject has been already alluded to when speaking of the hypothesis on the nature of the action of light;—it was shown that the amount of Iodide of Silver in the film should be proportioned to the energy of the rays and to the length of time they were allowed to act. Hence the effects of over-exposure are seen more quickly in the case of transparent films, than with others more dense in structure. There is reason however to think that the films employed by many Photographers are more dense and creamy than is really required; and if so, the gradation of tone would probably in most cases be improved by diminishing the amount of Iodide.

The author invariably finds that, with chemicals perfectly pure, a film one degree removed from the "blue opalescent," and possessing a silver-grey colour *with moderate translucency*, contains abundance of Iodide of Silver for Negative Portraits; but in the case of Landscapes, where the light of the sky is more powerful, it might be requisite to increase it somewhat.

C. MEANS OF INCREASING THE INTENSITY OF THE IMAGE IN COLLODION NEGATIVES.

To produce *intensity* in Negatives, we look more to the

proper management of the developing process than to any modification in the structure of the film.

For the sake of clearness, we may establish two stages in the development of a Collodion Negative;—first, *the development proper*, or bringing out of an image distinct in all its details by transmitted light, but pale and comparatively translucent; second, *the thickening* of this image, so as to make it darker and more opaque than before. The second stage of the development is the one with which we have now to deal.

The strengthening of a feeble image is effected by pouring over the plate a mixture of Pyrogallic Acid and Nitrate of Silver. These two substances decompose each other even without the aid of light, and a deposit of metallic Silver is formed *which settles down upon the image and adheres to it*. This fact has already been noticed in the third Section of the previous Chapter. It is a remarkable circumstance—for which we are not able to account—that the unaltered Iodide of Silver should be *unaffected* (if the materials are pure), and that the deposit of metallic Silver should adhere only to the image.

The addition of fresh Silver to the image in order to increase its intensity, is what Photographers term "pushing the development;" and it is curious and beautiful that it can be done in so uniform and perfect a manner, layer after layer of metallic particles being laid down without destruction to the gradation of tones in the Photograph.

The Collodion Iodide film, therefore, intended for Negatives, must be supplied with a proper amount of Nitrate of Silver during the development of the image. If this material falls short, no increased strength of reducing agent will add to the effect. There are two ways in which the required quantity of Nitrate may be added;—by increasing the strength of the Bath, or by mixing a few drops of

Nitrate solution with the developing agent immediately before using it.

Partial substitution of Acetate for Nitrate of Silver.—Mr. Hennah, of Brighton, whose Photographs are allowed by all to be of a superior description, attributes much of his success to the association of *Acetate* of Silver with the Nitrate. This might be supposed to act in two ways;—first, by ensuring the absence of *free Nitric Acid*, even when Collodion strongly tinted with Iodine was employed; and second, by facilitating the process of development, *Acetate of Silver being more easily reduced than Nitrate.*

It is certainly an advantage in the production of Negatives to remove all free Nitric Acid, not only from its retarding effects upon the exposure to light, but also on account of the injurious influence which it exerts on the *opacity* of the image. The addition of Acetate of Silver to the Bath substitutes *free Acetic Acid* for Nitric Acid, thus :—

Acetate of Silver + Nitric Acid.
= Nitrate of Silver + Acetic Acid.

Nitrite of Silver has also been recommended as well as Acetate, and it is probably due to the presence of one or both of these salts that a superior intensity is sometimes attributed to the use of "an old Nitrate Bath."

D. ON THE COLOUR OF NEGATIVES BY TRANSMITTED LIGHT AS INFLUENCING THEIR OPACITY TO THE CHEMICAL RAYS.

It is not by any means a safe plan to judge of the real intensity of a Negative Photograph,—that is, of its opacity to *chemical rays*,—by the appearance it presents when held up to the light. Such a course of procedure has probably in many cases led to the condemnation of a good Negative, which, if it had been tried, would have yielded the most brilliant Positive proofs. Negatives obtained *in a neutral*

Bath, and with a *small portion only* of Acetic Acid added to the Pyrogallic Acid, are of a *brown-yellow colour* by transmitted light, and comparatively translucent. On the other hand, those procured from a Bath containing Acetate of Silver, or with a *large quantity* of Acetic Acid added to the developer, appear of a dark bluish-black and considerably more intense than before. The difference however in the two cases is far more apparent than real, since the time taken in the subsequent printing process corresponds closely in each.

In a Bath containing Acetate of Silver, the colour of the Negative varies much with the length of time it has been exposed to light. The under-exposed proofs are jet black, the over-exposed of a dark ruby red. Probably, with the Nitrite and Oxide of Silver in the film a similar peculiarity would be observed.

Further Illustrations of the above remarks.— In employing solution of Chloride of Gold in order to strengthen Negative impressions,—although a deposit of Metallic Gold immediately forms and destroys the Positive appearance of the image, yet the apparent intensity by transmitted light is not greater than before. At the same time that Gold is deposited, an equivalent quantity of *Silver* is dissolved, so that the real thickness of the image remains unaltered. Nevertheless, as a change of colour to a greenish-yellow follows the deposition of the Gold, it is very possible that the chemical radiations may be obstructed to a greater extent than before.

The process of Professor Donny, presently to be described, affords a further illustration of the efficacy of brown-yellow tints in absorbing the actinic rays, as also does the Negative process of Mr. Maxwell Lyte, in which the image is converted into a *yellow* salt by treating it first with Bichloride of Mercury and afterwards with Iodide of Potassium.

E. ON THE PECULIARITIES OF PYROGALLIC ACID AND OF THE PROTOSALTS OF IRON EMPLOYED TO DEVELOPE NEGATIVE PHOTOGRAPHS.

Independently of a difference in strength or energy of action between the various developers, which was treated of in the last Chapter, there are other peculiarities of each still remaining to be noticed.

The characteristic of development by Pyrogallic Acid is that it takes place *in a continuous manner*, the image becoming more and more intense by degrees, as long as the supply of Nitrate of Silver is kept up.

The Sulphate of Iron, on the other hand, although it is capable of bringing out the impression under the most unfavourable circumstances in respect of acid and of Nitrate of Silver, does not so easily admit of the intensity being gradually increased in the way before described. It produces its full effect *quickly and at once*.

Probably these, as well as other differences, depend in great measure upon the nature of the acid, the Sulphuric, associated in the salt with the real developing agent, which is the *Protoxide* of Iron.

Mr. Hadow has indicated what appears to hold good both on theoretical and practical grounds, viz. that if any Protosalt of Iron is to take the place of Pyrogallic Acid in the development of Negative pictures, it will be the *Acetate*, in which the strong mineral acid is replaced by a weaker acid of vegetable origin.

F. ON THE MEANS EMPLOYED TO STRENGTHEN A FINISHED IMPRESSION WHICH IS TOO FEEBLE TO BE USED AS A NEGATIVE.

The ordinary plan of pushing the development cannot be applied with advantage after the picture has been washed and dried. In that case, if it is found to be too feeble to

print well, its intensity may be increased by one of the following methods.

It must be premised, however, that the same degree of excellence is not to be expected in a Negative Photograph which has been improperly developed in the first instance, *and more especially so if the exposure to light was too short.* Any "instantaneous Positive" may be rendered sufficiently intense for a Negative, but in that case *the shadows* are almost invariably *imperfect.* It is not in our power to lay down any lines or details which have not been properly impressed by light, and therefore we must be content to sacrifice a certain amount of gradation in tone.

1. *Treatment of the image with Sulphuretted Hydrogen or Hydrosulphate of Ammonia.*—The object is to convert the metallic Silver into *Sulphuret of Silver,* and if this could be done it would probably be of service. The Author finds however that the mere application of an Alkaline Sulphuret has little effect upon the image, excepting to darken its surface and destroy the Positive appearance by reflected light:—*the structure of the metallic deposit is too dense to admit of the Sulphur reaching its interior.*

Professor Donny (vol. i., 'Photographic Journal') proposes to obviate this by first converting the image into double Chloride of Mercury and Silver by the application of Bichloride of Mercury, and afterwards treating the white powder so formed with solution of Sulphuretted Hydrogen or Hydrosulphate of Ammonia. The structure of the double salt being spongy, receives the Sulphur well. Negatives produced in this way are of a brown-yellow colour by transmitted light, and opaque to chemical rays to an extent which would not, *à priori,* have been anticipated.

2. *MM. Barreswil and Davanne's process.*—The image is converted into Iodide of Silver by treating it with a saturated solution of Iodine in water. It is then washed, to

remove the excess of Iodine—exposed to the light—and a portion of the ordinary developing solution, mixed with Nitrate of Silver, poured over it. The changes which ensue are precisely the same as those already described; the whole object of the process being—*to bring the metallic surface back again into the condition of Iodide of Silver modified by light*, that the developing action may be commenced afresh, and more Silver deposited from the Nitrate in the usual way.

3. *The process with Bichloride of Mercury and Ammonia.*—Although this plan can scarcely be recommended as a very efficient one, yet as it involves some peculiar chemical changes, it may be well to describe it. The image is first converted into the usual white double Salt of Mercury and Silver by the application of a solution of the Corrosive Sublimate. It is then treated with Ammonia, the effect of which is to *blacken* it most intensely.—Probably the alkali acts by converting the Chloride of Mercury into the black Oxide of Mercury in the usual way. In place of Ammonia, a dilute solution of Hyposulphite of Soda may be used, with very similar results.

CHAPTER X.

ON THE THEORY OF POSITIVE PRINTING.

THE subject of Collodion Negatives having, it is hoped, been explained to the satisfaction of the inquirer, we proceed to show how, by means of them, an indefinite number of copies may be obtained, with the lights and shadows no longer reversed, but correct, as in nature.

Such copies are termed "Positives," or sometimes "Paper Positives," to distinguish them from direct Positives upon Collodion.

In general terms, we may say that there are two distinct modes of obtaining these Paper Positives;—first, by what is called the "*Negative process*," in which a layer of Iodide of Silver is employed, and the invisible image developed by Gallic Acid; and second, by the direct action of the light upon a surface of *Chloride of Silver*, no developer of any kind being used. The latter plan, as being the one commonly followed, will alone be alluded to.

The action of light upon Chloride of Silver was treated of in Chapter III. It was shown that a gradual process of darkening took place, and that the salt became reduced more or less completely to the metallic state,—that the strong affinity naturally existing between the two elements was broken up, and a separation of Chlorine resulted. At the same time it was also shown, that the rapidity and

perfection of the change was much influenced by the presence of excess of Nitrate of Silver, and of various organic matters, such as Starch, Lignine, etc. etc.

We have now to suppose that a "sensitive paper" has been prepared in this way, and that, a Negative having been laid in contact with it, the combination has been exposed to the agency of light for a sufficient length of time. Under these circumstances, on removing the glass, a Positive representation of the object is found below, of great beauty and detail. Now if this image were in its nature fixed and permanent, or if there were means of making it so without injury to the tint, the production of Paper Positives would certainly be the most simple department of the Photographic Art; for it will be found that with almost any Negative, and with sensitive paper however prepared, the picture will look well on its first removal from the printing-frame. The misfortune however lies here,—that the processes of fixing, which we are compelled to adopt in order to render the proof permanent, at the same time that they remove the unaltered Chloride and Nitrate of Silver, affect so much the appearance of the Photograph that its character is completely altered. The purple and violet tints, on which its beauty depended, at once disappear, and a dull, uniform brick-red takes their place.

It becomes necessary therefore to establish a fresh series of chemical operations in order to restore the brilliancy of the tint, and hence the consideration of the whole subject naturally divides itself into two parts;—first, the means by which the paper is rendered sensitive, and the image impressed upon it;—and secondly, the subsequent fixing and "colouring," as it is termed, of the proof. This latter division will be treated of first, the usual plan being adopted of describing the Chemistry before the Photographic action. Section I., therefore, is the Chemistry of the fixing and colouring Bath; Section II., its Photographic

action; and Section III., the preparation of the sensitive paper.

SECTION I.

Chemistry of the Fixing and Colouring Bath.

By "the colouring" of the Positive proof, is meant simply—*the imparting to it such tints as can be produced by the metals Gold and Silver, either alone or combined with Sulphur.*

The object has been, mostly, to find some solution which would both fix and colour at the same time. Plain Hyposulphite of Soda is not sufficient for this. It fixes the picture quickly and well, but, as before stated, leaves reddish tones which are not approved of.

M. Le Grey appears to have been the first to notice that the solution of Hyposulphite of Soda employed in fixing Positive proofs acquired a certain amount of colouring power by constant use, and that after the lapse of some time respectable purple and dark tints could be obtained. He attributed the improvement to the gradual accumulation in the Bath, of Salts of Silver dissolved out of the various proofs which had been fixed by it. Since then it has been usual to direct that in preparing a new Bath, Chloride of Silver should be added in convenient proportion.

Those however who adopted this plan, never found that it was immediately successful, and "an old Bath" has in consequence still been sought after as giving the best results.

The researches of the Author have, it is hoped, removed many of the difficulties which previously surrounded this part of the subject, and established the theory of the various changes which take place upon a more certain basis. It appears that, in order to construct a solution of the kind required, there exists a necessity for some chemical sub-

stance of *a more unstable nature* than the Hyposulphite of Soda, and this substance is supposed to act by imparting *Sulphur* to the proofs. The *Sulphuret of Silver* is much darker in colour than the Subchloride, and hence the tint is changed to black or some shade of brown more pleasing to the eye than the simple reduced Chloride.

This unstable substance, to which reference is made, is one of the members of the interesting series of the compounds of Sulphur with Oxygen, to which the term "Polythionic series" has been applied by Berzelius.

A fixing and colouring Bath then consists essentially of two distinct parts; first, the Hyposulphite of Soda; second, the Tetrathionate of Soda. To these a third may be added, although it is theoretically of minor importance, viz. the Hyposulphite of Silver. Each of these three constituents will be discussed separately, and afterwards the changes which ensue on mixing them together—or the Chemistry of the Bath in its complete state.

A. CHEMISTRY OF HYPOSULPHITE OF SODA.

This has already been treated of to a certain extent in Chapter V. There are however some few particulars not mentioned at that time which it will be useful to know.

One of these is, *the milkiness* which is immediately produced in Solution of Hyposulphite of Soda by the addition of any acid. Even the weaker vegetable acids, such as the Acetic, suffice to produce the effect. The explanation is as follows. *Hyposulphurous Acid*, which in combination with Soda forms the Hyposulphite of Soda, is an extremely feeble acid substance; hence when any ordinary acid is added to a solution of its salts, it is immediately displaced, the stronger acid taking to itself the base and uniting with it. The first effect then of adding "Acetic Acid" for instance to the Hypo solution is to form Acetate

of Soda and *free Hyposulphurous Acid*, both of which remain in solution.

But Hyposulphurous Acid is not only a body wanting in chemical energy, but it is also a very *unstable* substance. By its being *unstable* is meant that it is prone to spontaneous decomposition, its elements not having the power, so to speak, to hold themselves together; hence on being liberated from its combination with Soda, it does not remain in the liquid in a free state, but begins spontaneously to decompose and to pass into simpler and more stable combinations. Now the *composition* of Hyposulphurous Acid is represented thus:—

Sulphur 2 atoms; Oxygen 2 atoms.

Or in symbols— S_2O_2

Hence it is exactly equivalent to *Sulphurous Acid*, SO_2, and Sulphur, S.

The *milkiness* then which is produced by the addition of an acid to a Hypo solution is due to *Sulphur* in a finely divided state; and the odour similar to the fumes of burning Sulphur, perceived at the same time, is the Sulphurous Acid, both of these substances being products of the decomposition of Hyposulphurous Acid.

The mode of preparation usually adopted for Hyposulphite of Soda likewise illustrates the above fact. A *Sulphite* or combination of *Sulphurous Acid and Soda* is first formed, and afterwards the solution in water of this Sulphite is boiled with flowers of Sulphur until it is converted into a (Hypo)sulphite. SO_2 dissolves S and becomes S_2O_2.

Hyposulphurous Acid, although it is unstable when isolated, is comparatively fixed when combined with strong bases in the form of a salt. It is important to bear this in mind, because we shall almost immediately have to speak of bodies in which the reverse is the case.

B. CHEMISTRY OF THE POLYTHIONIC ACIDS AND THEIR SALTS.

The definite compounds of Sulphur and Oxygen were formerly considered to be but *four* in number, viz:—

	Formulæ.
Hyposulphurous Acid . .	S_2O_2
Sulphurous Acid	SO_2
Hyposulphuric Acid . . .	S_2O_5
Sulphuric Acid	SO_3

Of late years however three more have been discovered, which from the strong analogy in composition which they bear to the *Hyposulphuric Acid*, it was at first proposed to name *Sulphuretted* Hyposulphuric, *Bisulphuretted* Hyposulphuric, etc. Afterwards a less complicated nomenclature was adopted, and they were arranged together in a series, under the title of the "Polythionic Series" of Acids.

There are now therefore two distinct classes of Sulphur Acids:—the one including the Hyposulphurous, the Sulphurous, and the Sulphuric;—the other the Hyposulphuric and the acids of recent discovery.

a. *Composition of the Polythionic Acids.*—It is thus represented:—

	Sulphur.	Oxygen.	Formulæ.
Dithionic or Hyposulphuric Acid	2 atoms	5 atoms	S_2O_5
Trithionic Acid	3 ,,	5 ,,	S_3O_5
Tetrathionic Acid	4 ,,	5 ,,	S_4O_5
Pentathionic Acid	5 ,,	5 ,,	S_5O_5

The amount of *Oxygen* in all is the same, that of the other element increases progressively; hence it is at once evident, from a consideration of the formulæ, that the highest member of the series might *by losing Sulphur* descend by degrees until it reached the condition of the lowest.

b. *Instability of these Acids.*—All the Polythionic Acids

are *unstable*, with the exception of the Dithionic Acid. Their instability however varies much according to circumstances; in the case of the *Hyposulphurous Acid* we found that the acid itself was easily decomposed, but that when combined with an Alkali, as in the Hyposulphite of Soda, it was rendered comparatively permanent. With the Polythionic Acids however the reverse holds good, the acids themselves being invariably more stable than their salts. Not only so, but the stronger the base with which the acid is combined, the greater the instability; and a Polythionate of *Lead*—Oxide of Lead being a feeble base—will last a very much longer time than a Polythionate of Potash or Soda.

To illustrate further the foregoing remarks, it may be observed—that a solution of *pure Tetrathionic Acid* may be kept for a long time perfectly clear and transparent (and especially so if a little free acid of any kind, such for instance as the Acetic, be added to it), but if this Tetrathionic Acid be neutralized by addition of Carbonate of Soda, so as to convert it into the Tetrathionate of Soda, it begins after a few days to become milky from deposit of Sulphur, and when tested is found to contain a portion of *Tri*thionate, and even eventually of *Di*thionate of Soda.

c. *The acid reaction of Polythionates.*—In chemical language a salt is always termed *a neutral salt* when it contains one atom of acid to one of base; the Polythionates are therefore neutral salts, because they fulfil these conditions. But although neutral chemically speaking, they are not neutral to test-paper. A piece of Litmus paper immersed in solution of Hyposulphite of Soda remains unaffected, but if it is dipped in Tetrathionate of Soda, the blue colour is changed to red. There are many other salts besides the Polythionates, which possess the same peculiarity, but it is not necessary at the present time to allude to them.

d. *The action of Alkalies, or Carbonates of Alkalies, upon the Polythionates.*—By a careful examination of the formulæ it will be seen, that a Polythionate contains the elements of a *Hyposulphite* of the same base, and in addition, those of an atom of *Sulphuric Acid*. Now the action of a strong alkali upon a Polythionate is to cause a resolution of the salt into these two constituent parts, thus:—

Trithionate of Soda + *Potash*
= Hyposulphite of Soda + Sulphate of Potash.

The student will find it useful to bear this reaction in mind, as facilitating the comprehension of the effects produced by addition of caustic alkali to the colouring Bath.

e. *Theory of the various modes in which Polythionates may be prepared.*—The *Tetrathionic Acid* is certainly the most available for Photographic purposes, and therefore we direct our attention mainly to it in preference to the others. It may be prepared in either of the following ways:—

First, *By reaction of Sulphurous Acid upon Hyposulphite of Soda.*—Sulphurous Acid is that invisible gaseous substance of suffocating odour which results when Sulphur is burnt in air or oxygen. If this gas be conducted by means of a tube into a strong solution of Hyposulphite of Soda, it is rapidly absorbed, and its peculiar smell is communicated to the liquid. After standing however for twenty-four hours, the odour entirely disappears, showing that some decomposition has taken place. It is necessary that the Hypo solution should be concentrated, or the result does not follow.

The nature of the change may be stated thus:—

2 atoms Hyposulphite + 3 atoms Sulphurous Acid
= 1 atom *Tetra*thionate + 1 atom *Tri*thionate.

Second, *By reaction of Chloride of Gold, or Perchloride of Iron, upon Hyposulphite of Soda.*—When Chloride of

Gold is added to Hyposulphite of Soda, a solution is produced which contains *three* distinct salts, viz. Tetrathionate of Soda, Hyposulphite of Gold, and Chloride of Sodium, or common salt. The presence of the *Hyposulphite of Gold* in addition to the Polythionate, modifies the Photographic effect considerably, and hence it will be again alluded to.

Perchloride of Iron added to solution of Hyposulphite of Soda produces Tetrathionate of Soda and *Proto*chloride of Iron.

Fourth, *By action of Iodine upon Hyposulphites.*—This elementary substance dissolves freely in solution of Hyposulphite of Soda without production of colour. It is not however a case of mere solution, but of chemical decomposition. The Iodine removes an atom of Sodium, and by so doing it converts the Hyposulphite entirely into Tetrathionate: symbolically represented, the change is as follows:—

$$2\,NaO\,S_2O_2 + I = NaO\,S_4O_5 + NaI.$$

By examining this formula it is seen that *two equivalents* of any Hyposulphite contain the elements of *one* of Tetrathionate, *plus* an atom of metal; the Iodine unites with this metal, forming with it, in the case above given, Iodide of Sodium.

C. CHEMISTRY OF HYPOSULPHITE AND TETRATHIONATE OF SILVER.

Having discussed the Hyposulphite and Tetrathionate of Soda, it is necessary to say a few words on the nature of the corresponding salts of the same acids, with *Oxide of Silver* in the place of the Oxide of Sodium, or Soda.

It was shown in Chapter V. that when Chloride, Iodide, or Nitrate of Silver was dissolved in solution of Hyposulphite of Soda, the action was of a different kind from a common solution, such as that of salt in water,—that a

decomposition invariably took place, in virtue of which the Silver Salt, whatever its nature, was first converted into *Hyposulphite of Silver*, this Hyposulphite afterwards dissolving in the excess of Hyposulphite of Soda.

A solution of Hypo "containing Silver Salts" is therefore a solution of Hyposulphite of Silver in Hyposulphite of Soda. If this distinction is not borne in mind, it will be impossible to understand the changes which take place in such a solution, and to which reference is shortly to be made.

The Hyposulphite of Silver, if no excess of Hyposulphite of Soda is present, appears in the form of a white powder, which, being insoluble in water, precipitates to the bottom of the vessel.

a. *Instability of Hyposulphite of Silver.*—Hyposulphite of Silver is a *white* pulverulent substance when first formed, but it does not usually remain long in this state. It is liable to spontaneous decomposition, in the same manner as Hyposulphurous Acid and the Alkaline Polythionates. This decomposition sometimes takes place so rapidly that we see the whole process from beginning to end, even whilst the vessel containing the salt is still in the hand.

In order that the Student should bear this change in mind, he is recommended to perform the following experiment.

Let him take the Nitrate of Silver and Hyposulphite of Soda in equivalent proportions,—that is, about 21 grains of the former salt and 16 grains of the latter,—dissolving each, in separate vessels, in half of a fluid ounce of rain or distilled water.

These two solutions are to be mixed together rapidly and well agitated. Immediately a dense precipitate forms, which is Hyposulphite of Silver. At this point the curious series of changes commences. The precipitate, which

is at first white and curdy, after a short time becomes *canary yellow*, then of a rich orange yellow, afterwards liver colour, and finally *black*. The *rationale* of these changes is explained to a certain extent by studying the composition of the Hyposulphite of Silver.

The formula for this substance is as follows:—

$$AgO\ S_2O_2.$$

But $AgO\ S_2O_2$ plainly equals AgS, or Sulphuret of Silver, and SO_3, or Sulphuric Acid.

The black substance therefore into which the white Hyposulphite is eventually converted, is the Sulphuret of Silver. But what, it may be asked, is the nature of the *yellow* or *orange yellow* compound which is formed before the Hyposulphite becomes perfectly black? To this query no satisfactory reply can be given; the subject has not been examined so thoroughly as could be desired, and therefore we are constrained to be content with terming the yellow colour "the first stage of the decomposition of Hyposulphite of Silver."

b. *Circumstances which affect the stability of Hyposulphite of Silver.*—These are, practically speaking, of importance.

First, It may be said that the permanence of Hyposulphite of Silver is much increased *by dissolving it in Hyposulphite of Soda*. A solution of this kind may be kept for a very long time without any change in it being perceptible, although there is a tendency eventually to the production of a black precipitate, which is Sulphuret of Silver. The black Sulphuret of Silver does not dissolve in the Hyposulphite of Soda, and therefore as it forms it settles to the bottom of the bottle.

Secondly, The instability of Hyposulphite of Soda is increased by employing a soluble salt of Silver, like the Nitrate, in its preparation, in place of an insoluble salt, as the Chloride or Iodide. Nitrate of Silver and Hyposul-

phite of Soda seldom react upon each without some decomposition of the product; but Chloride of Silver is soluble to any extent without formation of black sulphuret.

Third, Concentration of both solutions concerned in its production favours the instability of Hyposulphite of Silver. If the Nitrate of Silver and Hyposulphite of Soda are very dilute, the white salt first formed dissolves in the excess without change of colour.

Fourth, Increase of temperature facilitates the decomposition. A very slight application of heat causes the blackening process to go on with rapidity.

c. *The Tetrathionate of Silver.*—This salt so strongly resembles the corresponding Hyposulphite, that it is not thought necessary to devote a separate division to the consideration of it.

Everything which has been said of the one may be applied also to the other. The Tetrathionate of Silver however, in passing into sulphuret, necessarily, from its composition, liberates *twice the amount of Sulphuric Acid* which the Hyposulphite does.

D. CHEMISTRY OF THE FIXING AND COLOURING BATH COMPLETE.

It may perhaps be thought that having discussed the Chemistry of each of the elements of the Bath taken separately, we are necessarily acquainted with its properties as a whole; such however is not the case, since *there are changes which ensue on mixing the various ingredients together*, and of these some notice must be taken.

a. *Change produced by mixing a Polythionate with solution of Hyposulphite of Soda.*—The Polythionates are all unstable salts, and easily decomposed by mixture with other reagents. If a small portion of Tetrathionate of Soda be poured into a solution of Hyposulphite of Soda, after the lapse of a short time a *milkiness* and deposit of

Sulphur takes place. The rapidity with which this is effected depends entirely upon the degree of concentration of the Hypo solution; if it is strong and nearly saturated, the change is speedy, and on the other hand, it is slower in proportion as the liquid is more dilute.

Judging from a previous knowledge of the properties of the Polythionates, we might be inclined to suppose that this slow and gradual precipitation of Sulphur, which continues for many days or even weeks, was due to a descent of some of the higher members of the Polythionic series to the condition of the lower,—that the *Tetra*thionate was losing Sulphur and becoming *Tri*thionate, or the *Tri*thionate passing by degrees to the state of *Di*thionate.

The reaction however is in reality more complicated than this, and it is seen to be so in the fact of *an acid substance* of some kind being formed.

Under the head of "Properties of Hyposulphites" it was mentioned that ordinary acids, such as Acetic, Sulphuric Acid, etc., could not long exist in solution of Hyposulphite of Soda, but that they tended to liberate Hyposulphurous Acid, and so to cause a milkiness of Sulphur, after which the liquid reassumed its neutral condition.

This acid however, formed by the reaction of Polythionates and Hyposulphite of Soda, whatever may be its nature, is certainly capable of existing for a long time in the liquid without causing any milkiness, and "an old Hypo solution" becomes at last permanently acid to test-paper.

b. *Changes produced in a solution of Hyposulphite of Silver in Hyposulphite of Soda.*—It has already been mentioned that the solution of Hyposulphite of Silver in Hyposulphite of Soda is comparatively permanent, and that the decomposition into Sulphuret does not take place under those circumstances with the usual rapidity.

Nevertheless, after the expiration of some days or weeks

a scanty deposit of black matter is found to have taken place, which is Sulphuret of Silver.

At present we have to notice—that supposing such a decomposition to have occurred either spontaneously or otherwise—with the separation of black matter is found also *a change in the properties of the supernatant liquid.* It contains a portion of *Sulphate* of Soda; but besides this it also contains *the same peculiar acid* before noticed as resulting from the mutual reaction of Tetrathionate and Hyposulphite of Soda.

Therefore we say that the decomposition of Tetrathionate of Soda, and of Hyposulphite of Silver, in contact with Hyposulphite of Soda, is probably of a similar kind, and that whatever is formed in the one case is also formed in the other.

If the student wishes to satisfy himself of the correctness of these observations, he may do so by proceeding in the same manner as before directed for the illustration of the changes in colour in decomposing Hyposulphite of Silver (see page 167), with this addition—that when the compound has reached the orange-yellow stage, half an ounce by weight of Hyposulphite of Soda, previously dissolved in half an ounce of water, is to be added, and the whole stirred and filtered.

The effect of this addition will be to dissolve a portion of the decomposing mass and to leave the rest in the state of black sulphuret. The solution becomes permanently acid to test-paper, and is found on trial to possess colouring properties in the same manner as if Tetrathionate had been added.

c. *Changes in a solution containing Tetrathionate of Soda, Hyposulphite of Silver, and Hyposulphite of Soda.* —A liquid containing these three ingredients is the colouring Bath complete, and the changes which take place in it are a combination of those recently described.

A considerable deposition of Sulphur first takes place, which is most marked soon after mixing, the acid reaction to test-paper manifesting itself at the same time.

After the expiration of some days or weeks, a slow formation of Sulphuret of Silver begins to be discerned, which adheres to the sides of the bottle in dense shining laminæ.

Eventually all deposition of any kind ceases, and the solution becomes useless until renewed by the addition of fresh Tetrathionate.

Experiment seems to show that the deposition of Sulphuret of Silver and also of free Sulphur takes place with greater rapidity when the solution is preserved neutral to test-paper. Therefore it is of importance, if it is intended to set aside the colouring Bath for some days or weeks, to render it slightly acid before doing so. A *neutralized* Bath however possesses the property of *spontaneously* regaining its original acid reaction, in process of time, by continued decomposition and formation of free acid.*

SECTION II.

Photographic action of the fixing and colouring Bath.

This subject may conveniently be divided as follows:—A. The ordinary phenomena of fixing and colouring a Positive proof.—B. The circumstances which affect the rapidity and perfection of the process.—C. Hypothesis on the exact nature of the change which takes place.—D. Explanation of the manner in which the efficiency of the Bath is maintained by the simple immersion of proofs.—E. On the use of Chloride of Gold in colouring Photographs.—F. On a peculiar effect produced by the presence

* Mr. Pollock states, that the deposition of Sulphur and Sulphuret of Silver, which results in the destruction of the colouring powers of the Bath, is much facilitated by the action of light, and that the solution should always be kept in a dark place when not required for use.

of Alkaline Iodides in the Bath.—G. On colouring by means of Hyposulphurous Acid.

A. THE ORDINARY PHENOMENA OF COLOURING A POSITIVE PROOF.

It was mentioned in the early part of this Chapter that the tint of the Positive proof, as seen on its removal from the printing frame, was warm and pleasing, but that this brilliancy, being of an evanescent character, immediately disappeared on immersion in the Hypo Bath.

The first effect produced by the colouring Bath is to dissolve away the free Nitrate of Silver upon the surface of the print, and also that portion of the Chloride of Silver which has not been acted upon by the Light. The tint of the picture at this early stage of this process varies much according to the manner in which the sensitive paper has been prepared, but the chemical composition of the surface may for practical purposes be considered to be always the same, viz. a *Subchloride of Silver*—that is, a salt containing less Chlorine than the ordinary Chloride of Silver. After the action of the Bath has been allowed to continue for a certain time, the colouring process is seen to commence; the reddish tints disappear by degrees, and various shades of purple take their place; eventually the colour becomes of a sepia-brown, or even of a pure black, and the process is at an end.

The chemical composition of the print after the coloration is complete, is different from what it was before; it is now a *Sulphuret of Silver*, or at all events a compound more or less approaching to Sulphuret in its characters.

Observe that during the whole process of colouring a gradual solvent action takes place upon the lighter shades of the proof. In consequence of this it is always necessary to print the picture some shades darker than it is intended to remain. The student will naturally suppose,

from his acquaintance with the peculiar properties of the Hyposulphite of Soda, that the solvent action is due to the influence of this salt. Such a view however is not altogether a correct one, since it will be found on trial that a *plain solution* of Hyposulphite of Soda of equal strength does not produce the effect to a similar extent. The solvent action is caused by the Hyposulphite and the colouring salt together, rather than by either of the two alone.

When the tint of the Photograph has reached a certain point, it does not improve, but rather deteriorates by prolonging the immersion in the Bath. It becomes of a dirty green hue, and the white portions of the image are changed to yellow. These facts are susceptible of being explained to a certain extent, and with that view they will again be brought before our notice.

B. CIRCUMSTANCES WHICH AFFECT THE RAPIDITY AND PERFECTION OF THE COLOURING PROCESS.

The colouring of a Positive Photograph proceeds in a gradual manner until it attains to a maximum. The amount of time however which is required to accomplish the change, and also the intensity of the colour when produced, varies much in different cases. The following circumstances will be mentioned as influencing the result:—acidity of the Bath—presence of Nitrate of Silver upon the surface of the proof—proportions of Hyposulphite and Tetrathionate—temperature of the solution—presence of Hyposulphite of Silver in the colouring Bath.

a. *Acidity of the Bath.*—A colouring Bath prepared with the Tetrathionates, is invariably acid to test-paper. It was shown in the last Section that the exact nature of the acid is not known, but that we are acquainted with the manner in which it is produced, viz. by the decomposition of Tetrathionate of Soda, or of Hyposulphite of Silver, or of both combined, in solution of Hyposulphite of Soda.

We notice now that if the acidity is carefully removed by the addition of Alkali in small proportion, taking care not to add an excess, the Photographic properties of the solution are modified thereby.

The Bath still produces coloration of the print, but it is more slow and gradual than before. There are however many advantages attending the employment of a neutral Bath. The tints, although lighter, are more warm and pleasing, and they are less apt to lose their brilliancy during the subsequent processes of washing and drying. The acid Bath also dissolves away the lighter shades of the print to a far greater extent than the neutral Bath, and hence the gradation of tone in the finished Photograph is inferior.

Thirdly, the neutral Bath allows of the print being immersed immediately on removal from the frame; whereas with the acid Bath, unless a portion of the free Nitrate of Silver is first removed, there is danger of a decomposition of Hyposulphite of Silver, and consequent yellow colour in the white portions of the proof.*

b. *Presence of free Nitrate of Silver upon the surface of the proof at the time of immersion in the Colouring Bath.* —The excess of Nitrate of Silver upon the surface of the proof when removed from the frame, greatly accelerates the rapidity and ultimate perfection of the colouring process. If the print is first soaked in salt and water in order to convert the Nitrate into *Chloride* of Silver, although it will still colour, yet the coloration takes place slowly and with difficulty. Photographers usually employ a much larger proportion of Nitrate of Silver in sensitizing paper than is actually required, and they do so because they find by experience that the excess assists the action of the colouring Bath, and produces dark tones in

* The yellowness does not invariably happen under the above circumstances even with an acid Bath, but the liability to it is decidedly increased

the print. The employment of very strong solutions of Nitrate of Silver however has the disadvantage of accelerating the change to a certain extent upon every part of the surface. Hence, at the same time that the dark parts are darker than before, the light parts are apt to be changed to yellow. If this yellow tint is objected to, the means of obviating it are threefold,—to keep the solution *neutral to test-paper*,—to remove the print from the Bath immediately the coloration is complete,—and third, to see that the solution contains a portion of Hyposulphite of Silver. The beneficial effects produced by the presence of a Salt of Silver in the colouring Bath will be again alluded to.

c. *Relative proportions of Hyposulphite and Tetrathionate used in preparing the Bath.*—A colouring Bath consists of a mixture of Hyposulphite of Soda and Tetrathionate of Soda, but the former salt is added in by far the larger quantity of the two.

Experiments show that the rapidity of coloration increases up to a certain point with the *strength* of the solution of Hyposulphite of Soda which is employed.

On the other hand, the amount of Tetrathionate required is comparatively small.

The rule is, that the colouring powers of the solution are improved by adding more Tetrathionate *only when a longer time is allowed to elapse before the mixed solution is used*. If the colouring Bath is to be employed within twelve hours after its first manufacture, probably it will not work in any way more quickly from an increase in the usual quantity of Tetrathionate having been made.*

d. *Temperature of the solution.*—This is practically important;—in very cold weather the Bath always works more slowly than usual, whereas in the height of summer,

* This rule does not apply to the Hyposulphite of Gold, employed as a colouring agent.

and especially in hot climates, it occasionally becomes quite unmanageable, from the rapidity and violence with which the various changes take place.

e. *Addition of Hyposulphite of Silver to the Bath.*—The essential elements of a colouring Bath include only Hyposulphite of Soda and Tetrathionate of Soda. The addition of a little Chloride or Nitrate of Silver however, so as to form Hyposulphite of Silver, is an improvement. The colouration is rather slower than before, but the tones are more decidedly purple and less of a grey colour than when no Silver is present. The tint of the proof does not suffer so much by prolonged immersion when the Bath contains Hyposulphite of Silver; also the clearness of the white parts is better preserved. No explanation of these facts is attempted; but they have been so frequently observed, that it is impossible to doubt their accuracy.

C. HYPOTHESES ON THE EXACT NATURE OF THE CHANGE WHICH TAKES PLACE IN THE COLOURING PROCESS, AND ON THE CHEMICAL COMPOSITION OF THE COLOURED SURFACE.

It has already been stated in general terms, that the process of colouring a Photographic proof consists essentially in imparting to it the element Sulphur, so as to form a Sulphuret of Silver, or a substance analogous to it in composition.

The Tetrathionates are all unstable bodies, tending continually to lose Sulphur, and to pass into the condition of *Tri*thionates. Nevertheless we can scarcely suppose that this is the *rationale* of the action of the colouring Bath, since there is reason to think that Tetrathionates are decomposed on mixing with Hyposulphites, and that the solution, when ready for use, contains a new principle distinct from any Polythionate. The most characteristic property of this principle is no doubt *instability, and a*

tendency to deposit Sulphur, in which respect it closely resembles the Tetrathionates, if not identical with them in composition.

Mode in which the Sulphur is imparted to the proof.—It is not easy to say whether the formation of Sulphuret of Silver takes place *directly*—that is, by the element being yielded at once to the reduced metal; or *indirectly*—by a preliminary formation and subsequent decomposition of a Hyposulphite, or a corresponding salt of Silver. There are arguments on both sides of the question,—for as, on the one hand, it is found that the colouration of the print is facilitated by all those causes which hasten the decomposition of Hyposulphite of Silver; so, on the other, it is evident that a principle exists in the solution containing much Sulphur loosely combined.

This is well shown by taking a colouring Bath prepared with the Perchloride of Iron, and adding to it a small quantity of Ammonia. Immediately a black precipitate forms, which is the *Sulphuret* of Iron. This fact is interesting, theoretically considered, because the tendency of Alkalies is to displace metallic *oxides*, and not metallic *sulphurets*.

If then we suppose that the darkened surface of reduced Chloride decomposes the unstable Sulphur compound existing in the Bath, in the same manner as the Ammonia and Iron Salt conjoined, the production of Sulphuret of Silver is at once explained.

Hypothesis on the Chemical Composition of the coloured surface.—Nothing can be stated with certainty on this point. It is however probable that the Sulphuret of Silver first formed afterwards combines chemically with the remaining Chloride, so as to form a double salt of the Chloride and Sulphuret of Silver. It has been shown that a *Chloro-sulphuret of Mercury* exists, of a colour different from either of the simple salts; and such being the case, it may be so also with Silver.

The Author, in experimenting roughly, succeeded in obtaining a substance of a brick-red colour, and possessing the following general characters:—unaffected by warm Nitric Acid—*blackened* by Ammonia and Hyposulphite of Soda; the Ammoniacal solution, on being tested, was found to contain Chloride of Silver, and the black powder proved to be Sulphuret of Silver. This therefore may have been a true double salt; but more accurate experiments are needed to establish such a fact beyond dispute.

D. ON THE MODE IN WHICH THE EFFICIENCY OF A COLOURING BATH IS MAINTAINED BY THE SIMPLE IMMERSION OF PROOFS, AND WITHOUT FRESH ADDITION OF TETRATHIONATE.

When a colouring Bath has been properly prepared, if it be kept in constant use, it will seldom be necessary to make any further addition of Tetrathionate. The solution contains within itself, to a certain extent, the means of its own renewal.

It was shown in the last Section that, whatever may be the precise nature of the substance possessing the colouring properties, it is certainly formed, amongst other methods, *by the decomposition of Hyposulphite of Silver* in contact with Hyposulphite of Soda.

Now each proof, on its immersion in the Hypo Bath, carries with it a layer of dried Nitrate of Silver upon the surface, and this Nitrate, in contact with the colouring solution, causes a certain amount of decomposition. The quantity decomposed is of course small, but it is sufficient for the purpose required, and serves amply to prevent the powers of the liquid from becoming exhausted.

If the plan of removing the free Nitrate by a preliminary immersion in plain Hyposulphite of Soda is adopted, then, in that case, the colouring Bath must be kept at a constant strength by occasional addition of fresh Tetrathio-

nate. So also, if the Bath be laid altogether aside for many weeks, until complete decomposition has taken place, the same artificial renewal will necessarily be required.

E. ON THE USE OF THE HYPOSULPHITE OF GOLD IN COLOURING PHOTOGRAPHIC PROOFS.

The addition of the Chloride of Gold to Hyposulphite of Soda produces, as before shown, both Tetrathionate of Soda and Hyposulphite of Gold (p. 166).

There is reason however to think that the latter of these two salts exercises the most important influence in modifying the tints. The quantity of Chloride of Gold used is always small, and would scarcely produce sufficient Tetrathionate to have much effect. Also it is found that the crystallized Sel d'Or, which is a double Hyposulphite of Gold and Soda freed from Tetrathionate, can be substituted for the Chloride without destroying the colouring properties.

The explanation of the action of Hyposulphite of Gold may be as follows.

Metallic Gold holds a position on the list of "chemical affinities" lower than that occupied by metallic Silver; that is, the latter metal has the greater *attraction for Oxygen*. In consequence of this superior affinity, Silver displaces Gold from its solutions in the same manner as it is itself displaced by other more oxidizable metals.

If you dip the polished blade of a knife in solution of Nitrate of Silver, a black deposit of metallic Silver is produced, and an equivalent quantity of Iron dissolved. So in the same way, a solution of Chloride of Gold poured upon a surface of pure Silver, deposits a crust of metallic Gold and takes up Silver in its place. It is conceived, then, that upon immersing a print in a Bath of Hyposulphite of Soda, containing Hyposulphite of Gold, a *substitution* of the one metal for the other takes place to a certain extent.

In experimenting in order to ascertain the capabilities of Hyposulphite of Gold of depositing metallic Gold upon a silvered surface, it was found to be much less energetic in that respect than the Chloride of Gold. A Collodion Photograph, treated with both in succession, became immediately covered with a grey crust in the latter case, but experienced no change until heated in the former. So again, a positive print immersed in dilute solution of Chloride of Gold is at once affected, but in Hyposulphite of Gold the change in colour may be deferred for many hours.

If we grant therefore that Gold is actually deposited, it becomes a question whether it remains in the condition of *metal*, or is subsequently converted into Sulphuret of Gold. The phenomena produced by immersing a print first in neutral Chloride of Gold and afterwards in Hyposulphite of Soda, are decidedly in favour of the latter view. The Hyposulphite of Soda, in that case, modifies the tint and makes it darker than before.

The greatest objection to the use of the Salts of Gold as colouring agents is the rapidity with which the Hyposulphite of Gold decomposes into Sulphuret. This Sulphuret of Gold, being insoluble in the Hypo solution, separates in shining scales, somewhat resembling the Sulphuret of Silver, but lighter in colour. Hence the quantity of Gold lost by decomposition is probably greater than that consumed in colouring the prints.

Observe also the manner in which a colouring Bath prepared with Chloride of Gold may by degrees alter its character completely, so as eventually to become identical with one prepared with the Tetrathionate. By a continued immersion of proofs, the products of decomposing Hyposulphite of Silver gradually accumulate, whilst at the same time the amount of Gold diminishes. Hence, after a time, the coloration is carried on by conversion of the reduced Chloride into *Sulphuret* of Silver in the usual

way, and is completed probably without any assistance from the Gold salt.

These changes in the general mode of action of the Bath take place more quickly in proportion to the number of proofs immersed and to the degree of concentration of the Hypo solution. It has already been shown that a strong solution of Hyposulphite of Soda reacts upon Nitrate of Silver and produces a colouring liquid far more quickly than a dilute solution. Hence in the formulæ given for preparing colouring Baths in Part II., the quantity of Hyposulphite of Soda directed to be used for a Gold Bath is less than that required for the Tetrathionate, the object being to retard as much as possible the generation of the sulphuretted colouring principle.

F. ON A PECULIAR INFLUENCE EXERTED BY ALKALINE IODIDES IN THE COLOURING BATH.

It was shown at an early period in the history of the Photographic Art, that the Iodides of the Alkalies, such as Iodide of Potassium or Ammonium, exerted a peculiar action upon the Chloride of Silver darkened by light;—that they tended, under certain circumstances, to bleach and remove the colour, and most probably so by supplying *Iodine* in place of the Chlorine which had been lost, and afterwards dissolving the neutral Iodide of Silver so formed in the excess of Alkaline Iodide.

A knowledge of these facts made it reasonable to suppose that an Iodide of a similar kind in the Hypo colouring Bath might be injurious, and accordingly experiments were made to determine whether such was the case. The results showed that *a large excess* of Iodide of Potassium or Sodium had the effect of dissolving the image completely away, and that a smaller quantity, whilst interfering slightly with the rapidity of coloration, tended also to cause a yellow deposit of Iodide of Silver in the lights.

These observations may be of service in suggesting the propriety of taking measures to remove the *Iodide of Sodium* always formed when Tetrathionates are produced by the action of Iodine upon Hyposulphite of Soda. In the practical directions for the preparation of colouring Baths this will be borne in mind, and directions given how to avoid the entrance of the Iodide into the Bath.

G. ON COLOURING POSITIVE PROOFS BY MEANS OF HYPOSULPHUROUS ACID.

The few remarks which it is proposed to offer under this head are not suggested with the idea of confusing the reader by needlessly multiplying facts, but simply to explain certain phenomena which he will probably meet with in the course of his experiments.

Photographers have long observed, that if a few drops of Acetic or Hydrochloric Acid be added to an old colouring solution which has become inactive, its energies are immediately restored to a considerable extent. This effect is not to be attributed to the acid itself, but rather to a *decomposition* set up by it in the liquid.

The Acetic Acid, on its addition, displaces an equivalent quantity of Hyposulphurous Acid, as was shown in the last Section, and this Hyposulphurous Acid immediately begins to split up into Sulphurous Acid and Sulphur. The decomposition, although it commences at once, is not thoroughly completed for some hours, and as long as it lasts, the colouring powers of the liquid continue.

This process with Hyposulphurous Acid is not in practice found to succeed so well as the other, but theoretically speaking it admits of comparison with it.

In employing the Perchloride of Iron or the Chloride of Gold in the preparation of Baths, the student will constantly find these remarks illustrated; both the Iron and Gold Salt, as they are usually sold, contain an excess of

free Hydrochloric Acid, which produces a milkiness in the Hypo solution more quickly than would result from employment of pure Tetrathionate.

The addition of *a larger quantity* of any acid, such for instance as the Sulphuric, to Hypo solution, produces a more permanent colouring effect; but in this case probably Tetrathionates, or the products of their decomposition, are formed; the Sulphuric Acid sets free *Hyposulphurous* Acid; the Hyposulphurous splits into *Sulphurous* Acid and Sulphur; the Sulphurous Acid reacting upon the excess of Hyposulphite of Soda, forms a mixture of Trithionate and Tetrathionate of Soda.

SECTION III.

Preparation of the Sensitive Paper.

It is not necessary to speak at the present time of the *general theory* of the preparation of a sensitive surface of Chloride of Silver, that subject having been already discussed in the Fourth Chapter of this work (p. 30).

There are some particulars however which relate to the condition of the surface of darkened Chloride, as affecting the rapidity and intensity of coloration, which it will be well to discuss.

Too much pains cannot be expended in the preparation of the sensitive paper, if rich and agreeable tones are desired in the resulting positive. The best of colouring Baths will only succeed well when the reduced salt is in the proper condition for undergoing the change. Remarks may be made upon the following subjects:—A. The colour of the print affected by the degree of reduction of the surface.—B. By the proportions of Chloride of Sodium and Nitrate of Silver used in sensitizing.—C. The use of Ammonio-Nitrate of Silver.—D. Of organic matters, Albumen and Gelatine.

A. THE COLOUR OF THE PRINT AFFECTED BY THE DEGREE OF REDUCTION OF THE SURFACE.

When we say that the darkened surface which forms the positive image is a Subchloride of Silver, it is not intended to assert that the composition of it is in all cases precisely the same. So far from that being the case, there are no doubt *stages* in the reduction of this salt; the Chlorine separating by degrees, and leaving a surface the composition of which is continually varying.

In like manner, as the chemical composition of darkened Chloride of Silver varies with the time of exposure to light, so also does the *colour* of the reduced surface. In order that the amateur may study these differences, he is to prepare a sheet of sensitive paper according to directions given in the Second Part of this work, and having cut it up into slips of a few inches square, to expose these slips to the bright sunlight for varying periods of time. At every visible change of colour, a slip is to be removed and laid aside in a dark place; eventually all are to be subjected to the action of the colouring Bath. The sequence of tints obtained by the simple action of Light will be as follows:—Pale violet—violet blue—slate blue—brown—chocolate brown—bronze, or copper-colour. On each of these the Hypo solution will produce a different effect.

The lightest shades dissolve away more or less completely. The intermediate ones first become lighter, and afterwards darken. The "bronze," or coppery metallic surface, the last stage of reduction of all, is very little affected; it neither dissolves, nor, for a long time, does it darken.

It is said that the intermediate shades darken; they do not however all do so to the same extent.—*The greatest depth and richness of colour is found with those which approach most nearly to the "coppery" stage.*

All this is important. As the solubility in Hypo diminishes, so, up to a certain point, does the depth and richness of colour increase. This point may be termed "the stage of complete reduction," when the deposit becomes metallic, and the whole or the greater part of the Chlorine is supposed to be separated.

With these facts before us, it is easy to understand that the tint of a Positive Photograph would be much influenced by the *density* of the Negative matrix from which it was produced. Pale and feeble Negatives cannot, by the most superior manipulation, be made to print well. The proofs are wanting in vigour, and have a flat and indistinct appearance. The reason of this is obvious:—The combination cannot be exposed to light for a sufficient length of time to bring about the requisite degree of reduction of the Chloride of Silver. Hence the deepest shadows of the resulting Positive are not sufficiently dark, and there is *a want of contrast* which is fatal to the effect.

A good Negative should be so opaque as to preserve the lights of the image beneath tolerably clear, *until the darkest shades were about to pass into the bronze or coppery condition.* If the amount of intensity is less than this, the finest tints procurable can scarcely be expected.

B. THE EFFECTS PRODUCED BY VARYING THE PROPORTIONS OF SALTS USED IN SENSITIZING.

It might seem at first that the quantities of both salts required for sensitizing could be easily deduced from a simple calculation,—that the atomic weight of Nitrate of Silver being about *three times* as great as that of Chloride of Sodium, therefore three times the strength of Nitrate would necessarily be required; this however is not altogether the case. Much depends upon *the length of time* that the salted paper is allowed to remain in contact with the Silver solution, and by a prolonged action the

decomposition is complete even with a weak Bath of Nitrate.

Nevertheless there are certain proportions both of salt and of Nitrate of Silver, which are found in practice to succeed better than others.

a. *Of Salt.*—As a general rule, it may be said that the *sensibility* of the paper is regulated up to a certain point by the amount of salt used in the preparation. The quantity of alkaline Chloride determines the amount of Chloride of Silver, and papers are more sensitive in proportion as they contain more Chloride of Silver.

Highly sensitized papers darken rapidly, and pass at length very completely into the *coppery* stage.

Weakly sensitized papers, on the other hand, darken more slowly, and are less apt to become coppery, even under the influence of a powerful light.

In practice it is found advisable to restrain the amount of Chloride of Silver within moderate limits, as the most sensitive papers are apt spontaneously to change colour, even in the dark.

b. *Proportion of Nitrate of Silver required.*—Provided the whole of the Chloride of Sodium be properly converted into Chloride of Silver, the sensibility of the paper is much the same whether the solution of Nitrate employed is strong or weak. It is necessary that an *excess* of Nitrate of Silver should be present to accelerate the action of light upon the Chloride of Silver; but when that excess is once established, nothing is gained by increasing it.

However, the employment of strong solutions of Nitrate of Silver in sensitizing Positive paper is usually recommended in Photographic works, from the superior richness of tone of the resulting proof. A surface of Chloride of Silver with a *bare excess* of Nitrate, such as would be produced by *brushing* a strongly salted paper with a Silver solution of moderate concentration, gives in the colour-

ing Bath a cold and flat tint, much wanting in depth and brilliancy. This subject has been sufficiently explained in the last Section (see p. 175).

C. THE USE OF THE AMMONIO-NITRATE OF SILVER.

The association of an alkali like Ammonia with Nitrate of Silver tends most powerfully to assist the reduction by light. It has been seen that the decomposition of the Chloride or Iodide of Silver with excess of Nitrate is attended *with the liberation of acid* (see page 46). This acid forms an impediment to the further continuance of the process, and the alkali acts by neutralizing it.

Chemistry of Ammonio-Nitrate of Silver.—Ammonio-Nitrate of Silver may be looked upon as a solution of the Oxide of Silver in Ammonia. It is produced by dissolving Nitrate of Silver in water, and dropping in Ammonia, until the brown precipitate first formed is taken up again. In a former Chapter, Oxide of Silver dissolved in *Nitrate of Ammonia*, was spoken of; this however is not the same compound as the one we are now considering. Although Nitrate of Ammonia is necessarily formed during the ordinary process of preparation of the Ammoniacal Oxide, yet its presence is not in any way necessary to the constitution of that substance, which is strictly speaking a solution of Oxide, not *in a salt of Ammonia*, but *in Ammonia itself*.

In the process of sensitizing salted paper by the Ammonio-Nitrate of Silver, *free Ammonia* is necessarily formed. When *plain* Nitrate of Silver is used, either Nitrate of Soda, or of Ammonia, is produced, both of which salts are neutral, and do not affect the result; but *Ammonia*, being a solvent for Chloride of Silver, must necessarily dissolve away a portion of the sensitive surface. Therefore, after the same solution of Ammonio-Nitrate of Silver had been employed many times, it would no doubt contain not only

Oxide of Silver, but also *Chloride* of Silver dissolved in Ammonia.

The following equation illustrates the difference in the two cases:—

Chloride of Ammonium + Nitrate of Silver
= Chloride of Silver + Nitrate of Ammonia.

Chloride of Ammonium + Oxide Silver in Ammonia
= Chloride of Silver + Ammonia + Water.

By the action of very strong solution of Ammonia upon Oxide of Silver, a black substance is obtained, termed "fulminating Silver," which possesses the most dangerous explosive properties. Its composition has not been accurately ascertained; but it is supposed by some to be a *Nitride of Silver,—id est*, a compound of Nitrogen gas with metallic Silver. The question has been raised, whether the ordinary solution of Ammonio-Nitrate of Silver might not possibly form this substance by spontaneous evaporation; but there is no reason to suppose that it would do so.

Photographic action of the Ammonio-Nitrate of Silver.—The first advantage gained by the employment of Ammonio-Nitrate is the same as that attributed to increased strength of the ordinary sensitizing solutions, viz. *a more rapid and complete reduction* under the influence of light.

But independent of this, it has other claims to our notice. The colour afterwards obtained in the Hypo Bath is peculiarly dark and rich with pictures prepared in this way. A velvety black in the shadows, and perfect integrity in the light portions of the proof, is certainly characteristic of Ammonio-Nitrate of Silver *when properly employed.*

Nevertheless it is most desirable, for reasons already given, to find a substitute for this preparation, and there can be but little doubt that the same effect might be pro-

duced by associating other substances—possibly of an organic origin—with the plain Nitrate of Silver ordinarily used in sensitizing.

D. THE EMPLOYMENT OF ORGANIC MATTERS, SUCH AS ALBUMEN, GELATINE, ETC.

Albumen has of late been much used in preparing Positive paper;—not so much for the sake of any advantage to be derived from it in the early part of the process or exposure to light, as for the improvement in appearance of the finished picture. It gives an agreeable gloss, and brings out the shadows and minor details with great distinctness.

Albumen pictures colour slowly in the Hypo Bath, and do not easily reach the darkest tints. A variety of purple and brown shades however may be obtained, very suitable for some subjects.

In Part III. of this work will be found a more detailed account of the nature of pure Albumen. From the account there given, it will be seen that it does not admit of the substitution of *Ammónio-Nitrate* for the ordinary Nitrate of Silver used in sensitizing.

Gelatine (see also Part III.) does not impart a gloss like Albumen, but it is useful in assisting to keep the solutions principally at the surface of the paper.

Dark tints may be obtained by Gelatine paper with or without Ammonio-Nitrate, and there is less tendency in the whites to become yellow than with Albumen.

CHAPTER XI.

ON THE PROPOSED SUBSTITUTION OF BROMIDES FOR IODIDES IN PHOTOGRAPHIC PROCESSES.

In the Daguerreotype process both *Iodine* and *Bromine* are employed conjointly,—and in that way a greater degree of sensitiveness is obtained, than by the use of either of the two alone.

It does not however follow that the same rule should apply to the Collodion film, since the two cases differ from each other so widely that they do not admit of comparison.

The observations which it is intended to make, may conveniently be included under the following heads:—A. The relative sensitiveness of Bromide and Iodide of Silver to white Light.—B. Superior sensibility of the former to coloured Light.—C. Division of the chemical rays of Light into two classes by means of Sulphate of Quinine.—D. Mode in which coloured objects are copied upon Iodide of Silver.

A. RELATIVE SENSITIVENESS OF BROMIDE AND IODIDE OF SILVER TO WHITE LIGHT.

It has long been a question with Photographers, whether the Bromide or the Iodide of Silver is the most sensitive to the influence of white Light. The general impression however appears to be in favour of the former. No doubt

much depends upon the physical structure of the films submitted to examination, and to the presence or absence of free Iodine in the Iodized Collodion employed. Bromized Collodion does not suffer the same decomposition by keeping as the Iodized, and hence it retains its sensitiveness for a longer period.

According to experiments roughly performed by the Author, it appeared that an opalescent neutral film of Collodio-Iodide of Silver was slightly more sensitive than any Bromide film which could be prepared. The difference however was not sufficiently great to make it a point of importance.

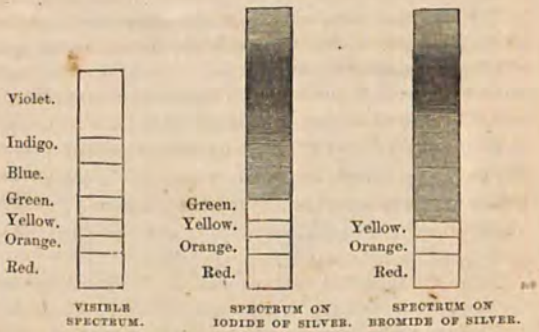
B. SUPERIOR SENSIBILITY OF BROMIDE OF SILVER TO COLOURED RAYS OF LIGHT.

It has already been stated (see p. 60), that the peculiar properties of white Light are associated each one with certain of the elementary coloured rays in preference to the others,—that the Blue, or the most refrangible, is the chemical ray, the Yellow the luminous, and the Red the heat-producing ray. Therefore, when the solar spectrum is allowed to impinge upon a prepared sensitive surface, the darkening characteristic of chemical action takes place only in the upper portions of the spectrum; the lower, or least refrangible part, being unaffected.

Observe however that there is a difference in this respect between a sensitive surface prepared with the *Iodide*, and one prepared with the *Bromide* of Silver.

The latter salt is affected more extensively,—that is, to a point lower in the spectrum,—than the former. In the case of the Iodide of Silver, the action ceases with the Blue space; but with the Bromide it reaches some way into the Green. The least refrangible colours—that is, the Yellow and Red—produce no effect either upon the Bromide or Iodide of Silver,—at least none that it is

necessary to take account of at present. The accompanying diagrams are intended to illustrate this.



Now it might appear at first that this superior sensibility of the Bromide of Silver to green rays of light must be a great advantage to the Photographer, seeing that tints of that kind are so abundant in Nature.

The author however has not been successful in the use of Bromide of Silver upon Collodion, and he believes that the opinion of the most eminent operators of the day is opposed to it. It can be shown too that even upon theoretical grounds we are not justified in expecting to derive that amount of benefit from the employment of Bromides which they might at first appear to promise; and for this reason—*that the rays with which Photographers at present work are not the coloured rays, but rather those near to or beyond the limits of the visible spectrum.*

The bearing which this statement has upon the question at issue, will be seen on reading what is immediately to follow.

C. SEPARATION OF THE CHEMICAL RAYS OF LIGHT INTO TWO CLASSES BY SOLUTION OF SULPHATE OF QUININE.

This must be looked upon as an arbitrary division, intended simply to facilitate the comprehension of the subject.

If the student will examine the two diagrams in the last page representing the action of the spectrum upon Iodide and Bromide of Silver, he will see that the darkening in both cases is by far the most decided at the upper part of the violet space and immediately beyond it; the chemical action is there exceedingly intense, and will produce a given effect in a very much shorter space of time than at any point lower down.

There are therefore, so to speak, in the solar spectrum certain actinic rays which are not associated with any visible colour, being more highly refrangible than all, and it is with these rays principally that Photographers work.

In order to gain a correct notion of the Photographic value of the "invisible" chemical rays, as compared with those which are associated with the upper coloured spaces, a simple plan is to select some medium which possesses the property of *absorbing* one set of rays and of permitting the other to pass; so that having sifted them out, as it were, the one from the other, we may be able to deal with each separately. Such a medium is distilled water holding in solution a large percentage of the *Sulphate of Quinine*.

A solution of the Sulphate of Quinine immediately strikes the most casual observer as being in some way different from ordinary liquids. It is perfectly colourless and transparent, like water, but has a peculiarly silvery and blue tinge when held in certain positions; hence it is easy to imagine that rays of white light are modified by passing through it. The nature of this modification is as follows:—the elementary coloured rays are all transmitted, consequently the fluid appears *colourless*, but *the most refran-*

gible chemical rays are absorbed. The white light which passes still possesses a certain amount of chemical action, but it is of that feeble kind which belongs more exclusively to the visible rays.

In the 'Journal of the Photographic Society,' vol. i., pages 86 and 100, will be found a detailed account of experiments on this subject, performed by Mr. William Crookes, to which the reader is referred for further information. At present it is intended to extract a statement which will illustrate the relative value of the *visible* and *invisible* actinic rays.

It was found that a picture upon *Bromized Collodion* required, when the Light was previously sifted by solution of Sulphate of Quinine, an exposure of *forty minutes;* upon Iodized Collodion, without the Quinine, *four minutes.* Therefore (supposing the sensibility of the two samples of Collodion to have been equal) by the employment of all the rays the image was formed in exactly a tenth part of the time required when only the coloured rays were used;—in other words, the invisible highly refrangible rays which affect both Bromide and Iodide of Silver alike, proved to be ten times more energetic than the coloured chemical rays which decompose the Bromide of Silver proportionably more.

To apply this argument then to the case originally supposed, viz. that of copying landscape scenery, where radiations of all kinds are present at the same time—what, it may be asked, would be the amount of effect produced by the green colour of the foliage, as compared with that of the other rays of white light? In point of fact, the picture might be taken *ten times over*, or somewhere thereabout, by all the rays conjoined, before these coloured rays would have time to impress themselves.

It is therefore probable that any advantage attendant on the use of Bromide of Silver—if such exists—is to be

attributed to other peculiarities possessed by that salt, and not to its superior sensibility to coloured light. If we could increase the sensitiveness of our chemical preparations to such an extent as to enable us to employ the Sulphate of Quinine Bath constantly for eliminating the more highly refrangible rays—then the state of the case would be entirely altered; but at present it is to these rays, and not to the others, that we must look for the impression of the image.

D. EXPLANATION OF THE MANNER IN WHICH DARK COLOURED OBJECTS IMPRESS IODIDE OF SILVER.

The following query may perhaps have occurred to the mind of the reader—If the coloured rays proceeding from natural objects produce no effect upon the sensitive surfaces, or so little that, practically speaking, it may be disregarded, how are these objects to be copied? To this the reply is, that they are delineated by means of the few and scattered rays of white light which are projected in some measure from the surfaces of all bodies, independent of their colour. *Pure homogeneous tints* are seldom found in nature, and even the darkest colours throw off a small proportion of the highly refrangible rays. The extent to which this takes place depends much upon the *power of reflecting light* possessed by the surface; and the amateur would soon discover this, even if not previously informed of it.

Hence it is that some kinds of foliage (as for instance the Ivy, with its smooth and polished leaf) are more easily copied than others. So again with regard to drapery—the *colour* of the material is not in any way more important than *the nature of its surface;* and a comparison in this respect between silks and satin on the one hand, and velvets and coarse stuffs of all kinds on the other, will abundantly demonstrate this to be the case.

CHAPTER XII.

ON THE CHEMISTRY OF THE DAGUERREOTYPE PROCESS.

It was not the intention of the Author, in writing the present work, to include any description of the Daguerreotype process.

The Daguerreotype is a branch of the Photographic art, so distinct from the others that, at least as far as manipulatory details are concerned, it can scarcely be said to bear any analogy to them. Still it is conceived that a slight sketch of the theory of this process may not be unacceptable to the amateur, who would naturally desire, whilst practising one department of the art, to escape from the imputation of being altogether ignorant of the outlines of another.

All necessary remarks to be made will fall under three heads:—A. The nature of the Daguerreotype film.—B. The means by which the latent image is developed.—C. The strengthening of the image by means of Hyposulphite of Gold.

A. THE NATURE OF THE DAGUERREOTYPE FILM.

The sensitive film of the Daguerreotypist is in many respects different from that of the Calotype or Collodiotype. The latter may be termed *wet processes*, in con-

tradistinction to the former, where aqueous solutions are not employed. The Daguerreotype film is a pure and isolated Iodide of Silver, formed by the direct action of Iodine upon the metal. Hence it lacks one element of sensitiveness possessed by the others, viz. the presence of the Nitrate or other soluble salt of Silver.

Details of the Process.—A copper plate of moderate thickness is coated upon the surface with a layer of pure silver, either by the electrotype or in any other convenient manner. It is then polished with great care, until the surface assumes a most brilliant metallic lustre. This preliminary operation of polishing is one of great practical importance, and the troublesome details attending it constitute one of the main difficulties to be overcome.

After the polishing is complete, the plate is ready for "the Iodine box," as it is termed,—that is, it is prepared to receive the sensitive coating. Now, to witness for the first time the process of iodizing a Daguerreotype plate cannot fail to prove to the amateur a most interesting event. He is perhaps sufficiently acquainted with chemistry to be aware, that the vapour of Iodine possesses a most magnificent purple colour, and therefore he expects to see the Iodine box under the application of a gentle heat, and filled with this beautiful vapour. Nothing of the kind however meets his eye,—he is shown *a simple piece of cardboard*, which appears discoloured, and has a peculiar smell from having been previously soaked in tincture of Iodine. This, he is told, is the source of the Iodine vapour, and immediately the operator proceeds to illustrate the fact by laying the cardboard upon a glass plate, and placing the silver tablet immediately above, the two surfaces facing each other, and separated by a very slight interval of about an eighth of an inch. After remaining for a short time, the plate is raised, and is found to have acquired a pale violet hue. The amount of Iodine

which produces this tint is so infinitesimally small, that it is probable, if the plate were laid in a balance, no difference in weight before and after would be detected.

The violet tint however is not what is desired, and consequently the silvered surface is again exposed for a short time to the action of the Iodine. The changes of colour which ensue under these circumstances are surprising and beautiful; they admit of comparison with nothing but the prismatic tints produced by the decomposition of white light by thin plates of mica, or by the surface of mother-of-pearl. From violet the plate becomes of a straw yellow—next rose-colour—and afterwards steel grey. By continuing the exposure still further, the same sequence of tints is repeated; the steel grey colour disappears, and the violet, yellow, and rose colours again recur. Of course, the deposit of Iodide of Silver gradually increases in thickness during these changes; but even to the end it remains excessively thin and delicate. In this respect it contrasts strongly with the dense and creamy layer often employed in the Collodion process, and shows clearly that a large proportion of the Iodide of Silver must in such a case be superfluous, as far as any influence produced by the light is concerned. We see at once, by looking at a Daguerreotype film, the microscopic nature of the actinic changes involved in the Photographic Art, and the lesson thereby learnt is a useful one to bear in mind.

Increase of sensibility obtained by combining the joint action of Bromine and Iodine.—The original process of Daguerre was conducted with the vapour of Iodine only; but in the year 1840 it was discovered by Mr. John Goddard that a mixed Iodide and *Bromide* of Silver was far more sensitive than the pure Iodide of Silver alone. It is therefore usual at the present time to expose the plate to both vapours—to the Iodine and to the Bromine in

succession,—the proper time for each being regulated according to the tint assumed by the plate.

The composition of this *Bromo-Iodide* of Silver, so called, is uncertain, and has not been proved to bear any analogy to that of the mixed salt obtained by decomposing a solution of Iodide and Bromide of Potassium with Nitrate of Silver. Observe also that the Bromo-Iodide of Silver is more sensitive than the simple Iodide *only when the vapour of Mercury is employed as a developer.* M. Claudet proves that if the image be formed by the direct action of light alone, the usual condition is reversed, and that the use of Bromine under such circumstances retards the effect.

The Daguerreotype and Collodion films compared with regard to sensitiveness.—There is reason to think that the Collodion process has slightly the advantage over the Daguerreotype in point of sensitiveness,—that a Positive image can be obtained upon a transparent neutral surface of Collodio-Iodide of Silver in a less time than would be occupied by the metal plate, even when the accelerating vapour of Bromine is employed.

B. THE DEVELOPMENT OF THE LATENT IMAGE IN THE DAGUERREOTYPE PROCESS.

The latent image of the Daguerreotype is developed in a manner altogether different from that of the humid processes generally—viz. by the action of Mercurial vapour. Mercury or Quicksilver is a metallic fluid which boils at 662° Fahrenheit. We are not however to suppose that the iodized plate is subjected to the vapour of Mercury at a temperature at all approaching to 662°. The cup containing the Quicksilver is previously heated by means of a spirit-lamp to about 140°, which is somewhat the degree of temperature easily borne by the hand, in most cases, without inconvenience.

The amount of vapour which rises from the surface of Mercury at 140° is of course small, but it is sufficient for the purpose, and after continuing the action for a few minutes the image is found to be perfectly developed.

Hypotheses on the chemical composition of the Daguerreotype image.—There are few questions which have given rise to greater discussion amongst chemists than the nature of the Daguerreotype image. Unfortunately, the quantity of material to be operated on is so small that it becomes almost impossible to ascertain its composition by direct analysis. There appears however but little doubt that it consists neither of metallic Silver nor of Mercury alone, but of both metals combined in the form of a *mercurial amalgam*. M. Claudet has shown that, by the application of a strong heat, Mercury can actually be volatilized from the image in sufficient quantity to develope a second impression immediately superimposed.

Therefore we may suppose that when the plate is placed in the developing box, the vapour of the Mercury attacks those portions which have been touched by light, and enters into combination with metallic Silver. The separated Iodine may perhaps again unite with a lower surface of the plate, but this is uncertain.

M. Claudet's discovery of the formation of a positive Daguerreotype image by the long-continued action of light alone without a developer.—It is a remarkable fact that an image more or less resembling that developed by Mercury can be obtained by *the prolonged action* of light alone upon the iodized plate. The substance so formed is a white powder, insoluble in solution of Hyposulphite of Soda; amorphous to the eye, but presenting the appearance of minute reflecting crystals when highly magnified. It may consist of pure metallic Silver, or of a Subiodide. This white salt cannot, apparently, be obtained by exposing the Collodio-iodide of Silver (previously washed to

remove the Soluble Nitrate) to light; and it is well known that Calotype papers are absolutely insensitive until excited with a solution of Nitrate of Silver. These facts, at the same time that they indicate peculiarities of some kind in the composition of the Iodized plate, also show the urgent need of further investigations on this intricate and difficult subject.

For all practical purposes the production of the Daguerreotype image by light alone is useless, on account of the length of time required to effect it. This was alluded to in the fourth Chapter, page 36, where it was shown that in the case of the Bromo-Iodide of Silver an intensity of light 3000 times greater was required, if the use of the mercurial vapour was omitted.

M. Ed. Becquerel's discovery of the continuing action of rays of yellow light.—Pure homogeneous yellow light has ordinarily no action upon a surface of Iodide of Silver; but if the Iodide is first exposed to white light for a sufficient time to impress a latent image, and then *afterwards* to the yellow light, the action already commenced is *continued*, and even at length to such an extent as to form the peculiar white deposit, insoluble in Hyposulphite of Soda, already alluded to.

Yellow light may therefore in this sense be spoken of as a *developing* agent, since it produces the same effect as the Mercurial vapour in bringing out to view the latent image.

A singular anomaly however requires notice, viz. that if the plate is prepared with the mixed vapours of Bromine and Iodine, in place of Iodine alone, then the yellow light cannot be made to develope the image. In fact, the same coloured ray which *continues* the action of white light upon a surface of *Iodide* of Silver, actually *destroys* it and restores the particles to their original condition with a surface of *Bromo*-Iodide of Silver.

These facts, although not of great practical importance,

are interesting in illustration of the delicate and complex nature of the chemical changes produced by light.

C. THE STRENGTHENING OF THE DAGUERREOTYPE IMAGE BY MEANS OF HYPOSULPHITE OF GOLD.

The use of the Hyposulphite of Gold to whiten the Daguerreotype image, and render it more lasting and indestructible, was introduced by M. Fizeau, subsequent to the original discovery of the process.

After removal of the unaltered Iodide of Silver by means of Hyposulphite of Soda in the usual way, the plate is placed upon a levelling stand and covered with a solution of Hyposulphite of Gold, containing about one part of the salt dissolved in 500 parts of water. The flame of a spirit-lamp is then applied until the liquid begins to boil. Very shortly a change is seen to take place in the appearance of the image; it becomes whiter than before, and acquires great force. This fact seems to prove conclusively that metallic Mercury enters into its composition, since a surface of pure Silver—such, for instance, as that of the Collodion image—is *darkened* by Hyposulphite of Gold, as before shown at page 181.

Also the difference in the action of the Hyposulphite solution upon the image and the pure silver surrounding it illustrates the same fact. This Silver, which appears of a dark colour, and forms the shadows of the image, is rendered still darker by the gilding process. A very delicate crust of metallic gold *gradually* forms upon it, whereas with the image the whitening effect is immediate and striking. Therefore it is reasonable to suppose that the finished image, after the gilding is complete, is a Mercurial Amalgam, containing both Gold and Silver.

PART II.

PRACTICAL DETAILS OF THE COLLODION PROCESS.

PRACTICAL DETAILS OF THE COLLODION PROCESS.

CHAPTER I.

PREPARATION OF THE MATERIALS REQUIRED IN THE COLLODION PROCESS.

In this Chapter it is intended to give the general details of the preparation of Collodion, and of the Nitrate Bath, etc., leaving the exact formulæ for the solutions until Chapter II.

All that relates to the subject of Photographic Printing, will be treated separately in Chapter V.

The division adopted may be as follows :—Section I. The Collodion.—Section II. The Nitrate Bath.—Section III. Developing and Fixing Liquids, etc.

SECTION I.

The Collodion.

This includes—A. The soluble Cotton.—B. The Alcohol and Ether.—C. The iodizing compounds.

A. THE SOLUBLE COTTON.

Pyroxyline may be prepared either from cotton wool or

from Swedish filtering-paper. A strong feeling has existed of late in the minds of many in favour of the latter substance, and there is no doubt but that it gives a product of very constant solubility, and yielding a fluid solution.* The cotton wool however is better adapted for use with the Sulphuric Acid and Nitre, since the paper, from its closeness of texture, requires a much longer immersion in the mixture.

Preparation of a Nitro-Sulphuric Acid of the proper strength.—There are two modes of preparing the Nitro-Sulphuric Acid: first, by mixing the acids themselves; second, by the Oil of Vitriol and Nitre process. The use of the mixed acids is decidedly advisable in all cases where large quantities of the material are operated upon at once; but when a small portion of soluble cotton is required, it can be made with less trouble by Sulphuric Acid and Nitrate of Potash.

PREPARATION OF NITRO-SULPHURIC ACID BY THE MIXED ACIDS.

The operator may proceed in either one of two ways: first, by taking the strength of each sample of acid, and mixing according to fixed rule; second, by a more ready but less certain plan, which may be used when the exact strength of the acids is not known. Each of these will be described in succession.

a. *Directions for mixing according to fixed rule.*—The formulæ for a definite Nitro-Sulphuric Acid of the proper strength for making the soluble Pyroxyline may be stated thus:—

* Swedish filtering-paper may be procured at the operative chemists, at about five shillings the quire. Each half-sheet has the water-mark "J. H. Munktell." It is said that the "papier Joseph" also succeeds well in the manufacture of soluble Pyroxyline.

	Atoms.	Atomic weight.
Nitric Acid	1	54
Sulphuric Acid . .	2	80
Water	6½	58
		192

In constructing such a formula, the first point is to ascertain accurately the specific gravity of both acids. Before performing this operation, it is necessary to observe that the *temperature* of the acid be accurately at 60° Fahrenheit, as the density of Sulphuric Acid, especially, is from its small specific heat greatly influenced by a change of temperature.

Having found the specific gravity of the acids, refer to proper tables (*vide* Appendix) for the percentage of *real acid* which is present. The following calculation will then give the relative weights of the ingredients required to produce the formula:—

Let $\begin{cases} a = \text{percentage of real Nitric Acid,} \\ b = \quad \text{,,} \quad \text{,,} \quad \text{Sulphuric Acid,} \end{cases}$

then $\frac{5400}{a}$ = quantity of Nitric Acid,

$\frac{8000}{b}$ = ,, Sulphuric Acid,

$192 - \frac{5400}{a} - \frac{8000}{b}$ = ,, Water.

Observe that the numbers in the calculation correspond to the atomic weights recently given, and that the amount of water is derived from the *total atomic weight*, viz. 192 *minus* the sum of the weights of both acids.

Hence if the samples of acid employed are too weak for the purpose, this is at once rendered evident by the formula for the water giving a negative quantity.

The weight of mixed acids produced by the formula is 192 grains, which would measure somewhere about two fluid drachms. Therefore ten times this quantity pro-

duces a convenient bulk of liquid, in which about 60 or 80 grains of paper may be immersed.

This calculation is deduced from Mr. Hadow's original paper in the 'Quarterly Journal of the Chemical Society,' vol. vii., page 201. The writer has seen it tried many times, and with invariable success, provided the materials were pure. It is possible however that in certain cases a mixture prepared by such a formula might be found to be *too weak*. This would result from the real strength of the two acids not corresponding accurately with the specific gravities. Oil of Vitriol commonly contains *Sulphate of Lead* (known by its becoming milky on dilution), and sometimes Bisulphate of Potash, both of which tend to raise the specific gravity. Nitric Acid is often strongly charged with the brown Peroxide of Nitrogen, and when such is the case the real strength of the acid is lower than is indicated. The combined effects of these impurities might perhaps produce an error equivalent to about four drops of water in the formula, or forty drops in the same multiplied ten times, as directed. The addition of three or four extra fluid drachms of Oil of Vitriol would probably restore the balance.

In weighing out corrosive liquids, such as Sulphuric and Nitric Acids, the operator is first to counterbalance a small glass in the scalepan, and then to pour in the acid carefully. If too much is added, the excess can be removed by a glass rod or by "the pipette" commonly employed for such a purpose.

If it is preferred to *measure* the acids, in place of ascertaining their weights in a balance, the following formula will give the number of fluid drachms required:—

Let $\begin{cases} a = \text{specific gravity of the acid,} \\ b = \text{its weight in grains,} \end{cases}$

then $\dfrac{b}{51{\cdot}7 \times a} = \text{number of fluid drachms;}$

54·7 grains representing the weight of a fluid drachm of distilled water.

The following example of a calculation similar to the above may be given:—

Specific gravity of the Oil of Vitriol, at 60° Fahr., 1·833.
Specific gravity of the Nitric Acid, at 60° Fahr., 1·448.

By a reference to Dr. Ure's Table of the Strength of Acids, these numbers are found to correspond to—

76·65 per cent. real Sulphuric Acid.
65·4 „ real Nitric Acid.

therefore $\frac{8000}{76{\cdot}65} = 104{\cdot}3$ grains of Oil of Vitriol.

$\frac{5400}{65{\cdot}4} = 82{\cdot}5$ „ Nitric Acid.

$192 - 104{\cdot}3 - 82{\cdot}5 = 5{\cdot}2$ „ Water.

Multiplying these weights ten times, we have—

Oil of Vitriol . . .	1043 grains.
Nitric Acid	825 „
Water	52 „
Total weight of the Nitro-Sulphuric Acid . . .	1920 grains.

Then, to reduce the weights in grains to fluid drachms

$\frac{1043}{54{\cdot}7 \times 1{\cdot}833} = 10{\cdot}4$ drachms of Oil of Vitriol.

$\frac{825}{54{\cdot}7 \times 1{\cdot}448} = 10{\cdot}3$ „ Nitric Acid.

$\frac{52}{54{\cdot}7} = 1$ „ Water.

Having prepared the acid mixture of a definite strength by the above formula, the operator may proceed to immerse the paper according to directions given at page 215.

b. *Plan for making Nitro-Sulphuric Acid, the specific gravity of the two acids not having been previously determined.*—Take a sample of Nitric Acid, as strong as can be obtained, and mix it with Oil of Vitriol as follows:—

Sulphuric Acid . . 10 fluid drachms,
Nitric Acid . . . 10 „

Then immerse a small tuft of cotton wool, and stir it in the mixture for five minutes. Remove with a glass rod, and wash with water for ten minutes, until no acid taste can be perceived.

If the tuft of wool becomes *matted*, and gelatinizes slightly on its first immersion, or if, in the subsequent washing, the fibres appear to adhere and to be disintegrated by the action of the water, *the Nitro-Sulphuric Acid is too weak*. In that case add to the acid mixture

Oil of Vitriol, 3 drachms.

If the cotton was actually *dissolved* in the first trial, an addition of as much as half of a fluid ounce of Oil of Vitriol may be required.

Supposing the cotton not to be gelatinized and to wash well, then wring it out very dry, pull out the fibres and treat it in a test-tube with rectified Ether, to which a few drops of Alcohol have been added. If it is *insoluble*, dry it by a gentle heat and apply a flame,—a brisk explosion indicates that the Nitro-Sulphuric Acid employed is *too strong*. In that case, add to the twenty drachms of mixed acids,

Water, 1 drachm,

or even $1\frac{1}{2}$ drachm if the compound was very highly explosive.

There is a third condition, somewhat different from either of the above, which is very puzzling to a beginner. It is this:—the fibres of the cotton mat together very slightly on immersion, but the washing proceeds tolerably

well,—the compound formed is scarcely explosive, and dissolves imperfectly in Ether, leaving little nodules or hard lumps, which are probably unaltered cotton. The ethereal solution yields, on evaporation, a film which is *opaque* instead of transparent. In this case, the acid mixture was slightly too weak, and the compound formed is Xyloidine, or analogous to it.

When the acid mixture has been brought to the proper strength by a few preliminary trials, proceed according to the directions given a few pages in advance.

PREPARATION OF NITRO-SULPHURIC ACID BY OIL OF VITRIOL AND NITRE.

This process is recommended, in preference to the other, to the amateur who is unable to obtain acids of any certain strength. The common Oil of Vitriol sold in the shops is often very good for Photographic purposes; nevertheless it is best, if possible, to take the specific gravity, and especially so if any doubt exists of its genuineness. At a temperature of 58° to 60°, specific gravity 1·833 is about the usual strength, and if it falls below this, it will be better to reject it. (See Part III. for 'Impurities of Commercial Sulphuric Acid.')

The Nitre should be the purest sample which can be obtained. Commercial Nitre often contains a large quantity of *Chloride of Potassium*, which is detected on dissolving the Nitre in distilled water, and adding a drop or two of solution of Nitrate of Silver. If a milkiness and subsequent curdy deposit is formed, Chlorides are present.

These Chlorides are certainly injurious; if in no other way, at all events, after the Oil of Vitriol is added, they destroy a portion of Nitric Acid by converting it into brown fumes of Peroxide of Nitrogen, and so alter the strength of the solution.

Therefore, if pure Nitrate of Potash, free from Chlo-

rides, can be obtained, the slight additional expense is not worth being taken into account; but if not, then the finest crystals of commercial Nitrate may be picked out, and will probably answer the purpose.

Nitrate of Potash is *an anhydrous salt;* that is, it contains simply Nitric Acid and Potash, without any water of crystallization; still, in many cases, a little water is retained mechanically between the interstices of the crystals, and therefore it is always better to dry it before use. This may be done by laying it in a state of fine powder upon blotting-paper, close to a fire, or upon a heated metallic plate.

Whether previously dried or not, the sample is *to be reduced to a very fine powder* before adding the Oil of Vitriol; if that precaution be neglected, portions of the salt escape decomposition, and the strength of the resulting Nitro-Sulphuric Acid is different from what is required.

Supposing these preliminaries to have been properly observed, weigh out—

Pure Nitre, powdered and dried, 600 grains.

This quantity is equivalent to 1¼ ounce Troy or Apothecaries' weight;—and to 1¼ ounce Avoirdupois weight *plus* 54 grains. Place this in a teacup or any other convenient vessel, and pour upon it

Water . . . 1⅛ fluid drachm
mixed with Oil of Vitriol . 12 „

Stir well with a glass rod for two or three minutes, until all effervescence has ceased, and an even pasty mixture, free from lumps, is obtained.

During the whole process, abundance of dense fumes of Nitric Acid will be given off, which must be allowed to escape up the flue or into the open air.

Slight modification of the formula required for commercial Nitre.—The above formula will invariably succeed

with a good sample of Oil of Vitriol and pure Nitre. When tried however with *commercial* Nitre, it failed in the writer's hands, the cotton being gelatinized and dissolved. Therefore in a second experiment the addition of water was altogether omitted, and the result proved satisfactory.

The following formula is also recommended by Mr. Hadow for employment with commercial Nitre :—

Nitre, powdered and dried .	510 grains.
Oil of Vitriol	15½ drachms.
Water	1½ drachm.

Observe that the quantity of Oil of Vitriol in this formula is much increased, to allow of the water being retained. The resulting mixture is very fluid and transparent, and the manipulation easy. The writer has seen this formula tried twice, with samples of common Nitre purchased at an oil-shop. In the first case the product was highly satisfactory, but in the second not quite so good, being only partially soluble and giving an opalescent film. In the latter case, probably, a better result would have been obtained by halving the quantity of water directed.

GENERAL DIRECTIONS FOR IMMERSING, WASHING, AND DRYING THE PYROXYLINE.

In the preparation of Nitro-Sulphuric Acid, it is important to notice the degree of heat which results on mixing the various ingredients together, as it is apt to vary considerably. Much of course depends upon the temperature of the atmosphere, but more upon the degree of concentration of the two acids ;—the rule is, that the stronger the Sulphuric Acid, and the weaker the Nitric Acid, the greater the evolution of heat. If the sample of Oil of Vitriol employed is good, the temperature on mixing will usually be about 130° with the acids, and 150° with the

Nitre.* Either of these will give a Pyroxyline yielding a fluid solution. But with a slightly dilute Oil of Vitriol the thermometer may indicate only 90°, or even less, and in that case the product would probably be the glutinous variety (see page 94). Therefore, before immersing the cotton, the cup containing the mixture may, in such a case, be floated for a short time upon the surface of hot water, until the requisite temperature is attained.

The Sulphuric Acid and Nitre requires to be used immediately after its preparation, as it solidifies into a stiff mass on cooling; the mixed acids, however, may be kept for any length of time in a stoppered bottle.

Cotton wool is best adapted for the Nitre process, but with the other the Swedish filtering-paper may be used. The fibres of the cotton should be well pulled out, and small tufts introduced singly, stirring with a glass rod in order to keep up a constant interchange of particles of acid.

The *quantity* of cotton must not be too great, or some portions will be imperfectly acted upon; about 20 grains to each fluid ounce of the mixture will be sufficient.

The *time of immersion required* varies from ten minutes with cotton, to twenty minutes or even half an hour with the paper. When an unusually large proportion of Sulphuric Acid is used, as in the formula given for the commercial Nitre, the cotton should be removed at the expiration of six or seven minutes, as it has been shown by Mr. Hadow that there is a greater tendency than usual to partial solution of the Pyroxyline under those circumstances.

After the action is complete, the acid mixture is left somewhat weaker than before, from addition of various

* In the preparation of soluble cotton, and indeed in all Photographic manipulations, a thermometer is almost indispensable. Instruments of sufficient delicacy for common purposes are sold in Hatton Garden and elsewhere, at a low price. The bulb should be uncovered, to admit of being dipped in acids, etc., without injury to the scale.

atoms of water necessarily formed during the change. Hence, if the same portion is used more than once, an addition of Sulphuric Acid will be required.

Directions for washing the soluble Cotton.—In removing the Pyroxyline from the Nitro-Sulphuric Acid, press out as much of the liquid as possible, and wash it rapidly in a large quantity of cold water, using a glass rod in order to preserve the fingers from injury. If it were simply thrown into a small quantity of water and allowed to remain, the rise in temperature and weakening of the acid mixture might do mischief.

The washing should be carried on for at least a quarter of an hour, or longer in the case of paper, as it is most essential to get rid of every trace of the acid. When the Nitre plan has been adopted, a portion of the *Bisulphate of Potash* formed adheres very tightly to the fibres, and if not carefully washed out, an opalescent appearance is seen in the Collodion resulting from the insolubility of this salt in the ethereal mixture.

If no acid taste can be perceived, and a piece of blue litmus paper remains in contact with the fibres for five minutes, without changing in colour, the product is thoroughly washed. Nevertheless, if the time can be spared, it is a safe plan to place the Pyroxyline in warm water and allow it to soak for several hours.

Lastly, wring it out in a cloth, pull out the fibres and dry by a gentle heat, always bearing in mind that the compound is more or less explosive, and therefore must not be brought too near to the fire. After drying, it may be kept for any length of time in a stoppered bottle. It has been stated on good authority that Pyroxyline is in some cases liable to a spontaneous decomposition, attended with evolution of red fumes of Peroxide of Nitrogen. This however must be rare, as the writer has not met with anything of the kind in the course of his experience.

RECAPITULATION OF THE GENERAL CHARACTERS OF PYROXYLINE PREPARED IN NITRO-SULPHURIC ACID OF VARIOUS DEGREES OF CONCENTRATION.

The acid mixture too strong.—The appearance of the cotton is not much altered on its first immersion in the mixture. It washes well, without any disintegration. On drying, it is found to be strong in texture, and produces a peculiar crackling sensation between the fingers, like starch. It explodes on the application of flame, without leaving any ash. It is insoluble in the mixture of Ether and Alcohol, but dissolves if treated with Acetic Ether.

The acid mixture of the proper strength.—No agglutination of the fibres of the cotton on immersion, and the product washes well; soluble in the ethereal mixture, and yields a *transparent* film on evaporation.

The acid mixture too weak.—The fibres of the cotton agglutinate, and the Pyroxyline is washed with difficulty. On drying, the texture is found to be short and rotten. It does not explode on being heated, but either burns quietly with a flame, leaving behind a black ash,—in which case probably it consists simply of unaltered cotton, or is only slightly combustible, and certainly not explosive. Treated with the ethereal mixture, it dissolves only *partially*, leaving behind lumps of unchanged cotton. The solution does not form an even transparent layer on evaporation, but becomes *opaque* and cloudy as it dries. This opacity however may be seen to a small extent with the best of soluble cotton, if the solvents contain too much water.

By studying these characteristics, and also by bearing in mind that the presence of about *a drachm and a half of water* in the quantities of acid given for the formulæ will suffice to cause the difference, it is hoped that the operator will easily overcome all difficulties.

B. PURIFICATION OF THE SOLVENTS REQUIRED FOR COLLODION.

Many, perhaps the majority, will prefer to buy both Ether and Alcohol in a state fit for use. Still a few hints on this subject may not be out of place.

The purity of the Ether employed is perhaps a matter of more importance in the manufacture of a good Collodion than that of any other ingredient. Unfortunately it is difficult to lay down with precision the exact nature of the injurious principles liable to be present.

There are three kinds of Ether ordinarily sold by manufacturing chemists; first, ordinary rectified Sulphuric Ether, as it comes from the distilleries, containing a certain percentage of Alcohol, and also of water; if it is good, the specific gravity is usually about ·750. Second, the washed Ether, which is the same agitated with an equal bulk of water, in order to remove Alcohol. By this proceeding the specific gravity of the fluid is reduced considerably. Third, Ether both washed and re-rectified, so as to contain neither Alcohol nor water; in this case the specific gravity is usually not higher than ·720.

The first of these commercial varieties is the one usually employed by Photographers, since it is sold at a lower price than the others; sometimes it is exceedingly pure and good, and is then to be preferred to the washed Ether; occasionally however this is not the case.

Some of the qualities which render Ether unfit for Photographic purposes, are as follows:—A. A peculiar and disagreeable smell either of some essential oil, or of Acetic Ether.—B. An acid reaction to test-paper.—C. A property of turning Alcholic solution of Iodide of Potassium brown with unusual rapidity.—D. A high specific gravity, from superabundance of Alcohol and water.

The Ether which has been both washed and redistilled

is always the most uniform in composition, and especially so if the second distillation was conducted from Quicklime or Caustic Potash. These Alkaline substances certainly remove many of the impurities, and leave the Ether in the best possible state for use.

The redistillation of Ether is a simple process, and therefore it will be described. In dealing with Ether however in any form, the greatest caution must be exercised, on account of its inflammable nature. Even in pouring Ether from one bottle into another, if a light of any kind be near, the vapour is apt to take fire; and severe injuries have been occasioned from this cause.

PURIFICATION OF ETHER BY REDISTILLATION FROM CAUSTIC POTASH.

Take ordinary rectified Sulphuric Ether and agitate it well with an equal bulk of water, in order to wash out the Alcohol; stand it for a few minutes until the contents of the bottle separate into two distinct strata, the lower of which—*id est*, the watery stratum—is to be drawn off and rejected. When this is done, introduce into the bottle Caustic Potash, finely powdered, in the proportion of about one ounce to a pint of the washed Ether; shake the bottle again many times, in order that the water—a small portion of which is still present in solution in the Ether—may be thoroughly absorbed. Afterwards set aside for twenty-four hours, at the end of which time it will probably be observed that the liquid has changed to a straw yellow colour, and that a flocculent deposit has formed in small quantity. Lastly, transfer the contents of the bottle to a retort of moderate capacity, supported in a saucepan of warm water, and properly connected with a condenser. On applying a gentle heat, the Ether distils over quietly, and condenses with very little loss; care must of course be taken that none of the alkaline liquid contained in the

body of the retort finds its way, by projection or otherwise, into the neck, so as to run down and contaminate the distilled fluid.

In order to preserve it from decomposition, it must be kept in stoppered bottles, quite full, and put away in a dark place. Also the stoppers should be tied over with bladder, or a considerable amount of evaporation will take place, unless the neck of the bottle has been ground with unusual care. After the lapse of some months, probably a certain amount of decomposition—evidenced by the liberation of Iodine from Iodide of Potassium—will be found to have taken place, in spite of all precautions. This however will be small in amount, and not of a character to injure the fluid, excepting for the most transparent varieties of film in which the amount of Iodide of Silver is reduced to a minimum.

PURIFICATION OF SPIRITS OF WINE BY RECTIFICATION FROM CARBONATE OF POTASH.

The object of this operation is to remove a portion of water from the spirit, and so to increase its strength. Alcohol thus purified may be added to Collodion almost to any extent, without producing glutinosity and rottenness of film.

The salt termed Carbonate of Potash is a "deliquescent" salt,—that is, it has a great attraction for water; consequently when Spirits of Wine are agitated with Carbonate of Potash, a portion of water is removed, the salt dissolving in it and forming a dense liquid which refuses to mix with the Alcohol, and sinks to the bottom. At the expiration of two or three days, if the bottle has been shaken frequently, the action is complete, and the lower stratum of fluid may be drawn off and rejected. *Pure* Carbonate of Potash is an expensive salt, and therefore a commoner variety may be taken. Even "Pearlash" (which

is a highly impure form of Carbonate) will succeed, if no better is to be procured.

The quantity of Carbonate of Potash used may be about an ounce and a half (or two ounces of the Pearlash) to half a pint of spirit; an excess however does no harm.

After the distillation is complete, a fluid is obtained containing about 90 per cent. of absolute Alcohol, the remaining 10 per cent. being water. The specific gravity at 60° Fahrenheit should be about ·823; commercial Spirit of Wine being ·836 to ·840.

C, PREPARATION OF THE IODIZING COMPOUNDS IN A STATE OF PURITY.

These are the Iodides of Potassium, Ammonium, and Iron, also the double Iodide of Potassium and Silver. The chemistry of each, and also that of Iodide of Cadmium, is more fully described in Part III.

a. *The Iodide of Potassium*—Iodide of Potassium, as sold in the shops, is often contaminated with various impurities. The first and most remarkable is *the Carbonate of Potash*. When a sample of Iodide of Potassium contains much Carbonate of Potash, it presents itself in the form of small and imperfect crystals, which are strongly alkaline to test-paper, and *become moist on exposure to the air*, from the deliquescent nature of the Alkaline Carbonate. The solution of these crystals in common Alcohol has also an alkaline reaction; but if the strong Alcohol be employed, then the impurity is not dissolved to an appreciable extent.

Sulphate of Potash is another salt frequently found in the Iodide of Potassium. It is not soluble in strong Alcohol. The proper test for detecting a soluble Sulphate is the Chloride of Barium (see Part III., article Sulphuric Acid). Commercial Iodide of Potassium however is rarely so pure that no change whatever is produced by Chloride

of Barium; therefore a mere *opalescence* or slight milkiness on the addition of that salt may be disregarded, but if a decided white precipitate is formed (insoluble in Acetic Acid), it will be better to reject the sample, or to purify it by solution in strong Alcohol.

A third impurity of the Iodide of Potassium is the *Chloride of Potassium*; but as the presence of this salt is not so readily detected, the best means of avoiding it is to purchase the Iodide of a manufacturing chemist who can be depended upon for purity of the materials he supplies.

The test for Alkaline *Chloride* in a solution of Iodide of Potassium, is as follows:—Precipitate the salt by an equal weight of Nitrate of Silver, and treat the yellow mass with solution of Ammonia; if any Chloride of Silver is present, it dissolves in the Ammonia, and after filtration is re-precipitated in white curds by the addition of an excess of pure Nitric Acid. If the Nitric Acid employed is not pure, but contains traces of free Chlorine, the Iodide of Silver must be well washed with distilled water before treating it with Ammonia, or the excess of free Nitrate of Silver dissolving in the Ammonia would, on neutralizing, produce Chloride of Silver, and so cause an error.

b. *The Iodide of Ammonium.*—This salt may be prepared by adding Carbonate of Ammonia to Iodide of Iron, but more easily by the following process. A strong solution of Hydrosulphate of Ammonia is first made, by passing Sulphuretted Hydrogen gas into Liquor Ammoniæ. To this liquid Iodine is added until the whole of the Sulphuret of Ammonium has been converted into Iodide. When this point is reached, the solution at once colours brown from solution of free Iodine. On the first addition of the Iodine, an escape of Sulphuretted Hydrogen gas and a dense deposit of Sulphur take place. After the decomposition of the alkaline *sulphuret* is complete, a portion of Hydriodic Acid—formed by the mutual reaction of

Sulphuretted Hydrogen and Iodine — attacks any Carbonate of Ammonia which may be present, and causes a lively effervescence. The effervescence being over, the liquid is still acid to test-paper, from excess of Hydriodic Acid; it is to be cautiously neutralized with Ammonia, and evaporated by the heat of a water-bath to the crystallizing point.

The crystals should be thoroughly dried over a dish of Sulphuric Acid, and then sealed in small tubes containing each about half a drachm of the salt.

The writer invariably employs the Iodide of Ammonium for the purpose of iodizing Collodion, and finds that at the expiration of fourteen months from the time of preparation it is still perfectly colourless.

Iodide of Ammonium is very soluble in Alcohol, but it is not advisable to keep it in solution, from the rapidity with which it decomposes and becomes brown.

c. *The Iodide of Iron.*—Iodide of Iron, in a state fit for Photographic use, is very easily obtained by dissolving about a drachm of Iodine in an ounce of "proof spirit,"—that is, a mixture of equal bulks of Spirits of Wine and water,—and adding an excess of iron filings. After a few hours, a green solution is obtained without the aid of heat. The presence of metallic iron in excess prevents the solution in a great measure from decomposing, as it would otherwise speedily do.

d. *Double Iodide of Potassium and Silver.*—In preparing this compound, first form Iodide of Silver, by dissolving equal weights of Iodide of Potassium and of Nitrate of Silver in separate portions of rain or distilled water, and washing the resulting yellow precipitate upon a filter. The washing is to be conducted, first, with water to wash away the Nitrate of Soda, and afterwards with a small portion of Alcohol to displace the water.

Then digest the yellow mass with excess of Iodide of

Potassium in Spirits of Wine, until a saturated solution of the double salt is obtained.

An analysis of a saturated solution of double Iodide of Potassium and Silver in Alcohol of specific gravity ·836, gave, as the quantity of both salts present in one fluid ounce,

Iodide of Potassium 64 grains,
Iodide of Silver . . 24 ,,

Therefore, 1½ drachm of powdered Iodide of Potassium, and about 20 grains of Iodide of Silver, obtained by precipitating 15 grains of Nitrate of Silver by an equal weight of Iodide of Potassium, may be digested for some hours in an ounce of the Spirits of Wine.

SECTION II.

The Nitrate Bath.

In this Section, the most convenient methods of saturating the Bath with Iodide and Carbonate of Silver will be described: also,—B. the conversion of a portion of the Nitrate into Acetate of Silver; and—C. the means of rendering the solution chemically neutral.

A. SATURATING THE BATH WITH IODIDE AND CARBONATE OF SILVER.

a. *With Iodide of Silver.*—The general theory of the manner in which a Nitrate Bath is saturated with Iodide of Silver was described at page 102.

A concentrated solution of the Nitrate of Silver is first prepared, and to this a small portion of Iodide of Potassium is added; the yellow precipitate dissolves in the strong solution, but on diluting with water, the double salt so formed is decomposed, and a portion of Iodide of Silver is precipitated, leaving the solution perfectly saturated.

The following directions will apply in all cases, excepting where the strength of the Bath is to be above 40 grains of Nitrate of Silver to the ounce:—

Dissolve the whole quantity of Nitrate of Silver advised in the formula, in about *two* parts of water; then take Iodide of Potassium 1½ grains to each 100 grains of Nitrate, dissolve in half a drachm of water, and add to the other; a yellow deposit of Iodide of Silver is first formed, which, on stirring, completely redissolves. The concentrated solution is then diluted with water to the required bulk (stirring all the time), and afterwards filtered from the milky deposit. If the liquid does not at first run clear, it will usually do so on passing it through the same filter a second time.

b. *Saturating the Bath with Carbonate of Silver.*—As the quantity of free Nitric Acid contained in crystals of Nitrate of Silver varies so much, it is always best to commence by adding Carbonate of Soda until the whole of it is removed. To do this, take of common washing Soda 1 grain to each 100 grains of Nitrate of Silver, and add it, dissolved in half a drachm of water, to the solution of Nitrate. If a permanent milkiness is produced, a sufficient excess has been added; but if, on the other hand, the white precipitate of Carbonate of Silver first formed is redissolved on stirring, free Nitric Acid is still present, and a further quantity of the Soda must be used.

In order to save the trouble of two filtrations, it is better to add the carbonate of Soda to the concentrated solution of Nitrate at the same time with the Iodide of Potassium, and afterwards to dilute down to the proper bulk, when the excess of Iodide of Silver and of Carbonate of Silver will be separated.

B. CONVERSION OF A PORTION OF THE NITRATE OF SILVER INTO ACETATE OF SILVER.

It has been recommended, at page 153, in the preparation of a Nitrate of Silver Bath to be used for Negatives, to add to it a portion of Acetate of Silver. This may be easily effected in the following simple manner. Take of the ordinary Carbonate of Soda used for washing (the composition of the Sesquicarbonate employed in making effervescing draughts is different;—see Part III. "Carbonate of Soda") the same weight as that given in the formula for the Acetate of Silver (*vide* p. 246, next Chapter), dissolve it in a drachm or two of water in a test-tube, and drop in glacial Acetic Acid until a piece of immersed test-paper becomes reddened. Then add the liquid, which is a solution of *Acetate of Soda*, to the Bath.

Acetate of Soda, added to Nitrate of Silver, produces probably, by double decomposition, Acetate of Silver and Nitrate of Soda; at all events, the photographic action is the same as if the crystallized Acetate of Silver had been employed.

As the atomic weights of crystallized Carbonate of Soda and of Acetate of Silver are not very different, any quantity of the former represents about an equal weight of the latter.

C. RENDERING THE BATH CHEMICALLY NEUTRAL.

The simplest plan of making a chemically neutral Bath, is to take the crystals of Nitrate of Silver, and before dissolving, to heat them to a point just short of fusion, so as to drive off any excess of free Nitric Acid which may be present. This operation can be conducted in a hot-air bath, the temperature being maintained at 300° to 350° for an hour or more.

If the salt however is already in solution, the operation

of neutralizing becomes more difficult. It is almost impossible to add a portion of alkali exactly sufficient, without incurring any excess, and an excess of alkali produces Oxide of Silver, which renders the Bath alkaline to test-paper.

The best plan of proceeding in that case is to prepare two solutions of a given strength, such as are termed by chemists "standard solutions," viz. a solution of alkali and a solution of acid, so constructed that a single drop of the one neutralizes precisely one drop of the other.

Mode of preparing standard solutions of Nitric Acid and alkali; the acid to contain $\frac{1}{10}$th of a grain of real Nitric Acid in a minim.—The first point is to select an alkali the composition of which is tolerably uniform. The "Bicarbonate of Potash" answers very well; it is a pure crystallized salt, and can be purchased at any druggist's shop.

Take about half an ounce of the Bicarbonate and reduce it to powder, to procure a uniform mixture. Then weigh out exactly 90 grains, and dissolve in one ounce of rain or distilled water. Next dilute down half of a fluid ounce of Nitric Acid, of the common strength, with three ounces of water.

Place the solution of Bicarbonate in a capsule and apply a gentle heat (the object of heating is to facilitate the escape of the Carbonic Acid gas generated upon addition of the Nitric Acid). If a capsule is not at hand, a teacup will do as well, floated upon the surface of boiling water.

Pour in the acid gently, with constant stirring. When the effervescence begins to be less violent than at first, which will probably happen after the addition of about three-quarters of a fluid ounce of the diluted acid, place a few strips of blue litmus-paper in the liquid, and continue the process carefully, drop by drop. The evolved Carbonic Acid gas changes the colour of the paper to a

reddish purple, but the addition of Nitric Acid must not be discontinued until a *decided red tint* is obtained. When this is the case, read off exactly the bulk of diluted acid which has been employed, and measure out an equal quantity as representing the amount of acid corresponding to 90 grains of Bicarbonate of Potash. Now 90 grains of Bicarbonate of Potash are neutralized by 48 grains of real Nitric Acid; consequently, if the measured quantity of acid be diluted with distilled water to two fluid ounces, we obtain a standard solution, each minim of which represents $\frac{1}{20}$th of a minim of anhydrous Nitric Acid.

To prepare the standard alkaline solution, it is only necessary to dissolve 90 grains (being the same quantity as before) of the Bicarbonate of Potash in two fluid ounces of water.

Although the description of this process is somewhat tedious, the manipulatory details involved in it are exceedingly simple; and the facility of working the Bath is so much increased by the possession of alkaline and acid solutions of definite strength, that their employment is by all means to be recommended.

A more simple process for preparing equivalent alkaline and acid solutions.—Take common Nitric Acid and dilute it with twenty times its bulk of water; then drop in Ammonia into a measured quantity, drop by drop, until the colour of the immersed litmus paper changes from red to blue. Note the measure of Ammonia required to produce neutralization, and dilute a corresponding amount to the same bulk as the acid.

In this simple manner two solutions are obtained, equivalent to each other; but they can scarcely be termed standard solutions, since the strength of the Nitric Acid taken for dilution is uncertain.

SECTION III.

The developing and fixing liquids.

A very few words on this head will suffice. The substances ordinarily used for developing the image, and also the fixing agents, are to be purchased in the solid form. Hence nothing is required but to dissolve in rain or distilled water, and to pass the solutions through filtering-paper. Even the trouble of filtration may often be avoided, if the liquid is found to be tolerably clear and free from suspended particles of solid matter.

The Protonitrate of Iron, however, forms an exception. It cannot be preserved in the crystalline form, and must therefore be prepared in small quantities at a time, as required for use.

PREPARATION OF THE PROTONITRATE OF IRON.

There are two processes commonly followed for preparing the Protonitrate of Iron.

The first is by the action of dilute Nitric Acid upon the Sulphuret of Iron. Dilute an ounce of Nitric Acid with six ounces of water, and add to it about half an ounce of Sulphuret of Iron, previously broken into very small fragments. Set the vessel aside for several hours, in a place where the offensive and poisonous Sulphuretted Hydrogen gas may escape without doing injury. When all effervescence has ceased, pour off the green solution, add to it 20 grains of powdered chalk or whiting, and boil it in a flask for five minutes. Allow to cool, and filter from the black deposit, if any has formed.—In this process the Nitric Acid, being in a diluted state and employed cold, does not act as an oxidizing agent, but simply displaces Sulphuretted Hydrogen and forms Protonitrate of Iron. The chalk is added, in order to neutralize a small portion of free Nitric Acid, which commonly remains after the action is

complete. If a black deposit is noticed on boiling, it is *Sulphuret of Iron* produced by the excess of Sulphuretted Hydrogen, dissolved in the liquid, again reacting upon the Protosalt of Iron as the solution becomes neutral.

Preparation of Protonitrate of Iron by double decomposition.—This plan is the one originally employed by Dr. Diamond. It is somewhat less economical than the last, but probably superior to it in most other respects.—Take of Nitrate of Baryta 300 grains;—powder and dissolve by the aid of heat in three ounces of water. Then throw in by degrees, with constant stirring, crystallized Sulphate of Iron, *powdered*, 320 grains. Continue to stir for about five or ten minutes. Allow to cool, and filter from the white deposit, which is the insoluble Sulphate of Baryta. The reaction is explained thus:—

Nitrate of Baryta + Sulphate of Iron.
= Sulphate of Baryta + Nitrate of Iron.

In place of Nitrate of Baryta, the Nitrate of Lead may be used (Sulphate of Lead being an insoluble salt), but the quantity required will be different. The atomic weights of Nitrate of Baryta and Nitrate of Lead are as 131 to 166; consequently 300 grains of the former is equivalent to 380 grains of the latter.

CHAPTER II.

FORMULÆ FOR SOLUTIONS REQUIRED FOR COLLODION PHOTOGRAPHS.

SECTION I.—Formulæ for direct Positive Solutions.
SECTION II.—Formulæ for Negative Solutions.

SECTION I.

Formulæ for Positive Solutions.

Two processes will be given for obtaining glass Positives;—the first, a process perfected by the author, and described in the 'Journal of the Photographic Society,' vol. i.; the second, the ordinary Positive process, easier to practise than the last, but considerably less sensitive, and more uncertain in the results.

The solutions are taken in the following order:—A. The Collodion.—B. The Nitrate Bath.—C. Developing fluids.—D. Fixing liquids.—E. Whitening solution.

SENSITIVE POSITIVE PROCESS WITH NEUTRAL FILMS.

A. THE COLLODION.

Purified Ether, sp. gr. ·720 . . .	5 drachms.
„ Alcohol, sp. gr. ·825 . . .	3 „
Soluble Cotton	1½ grains.
Pure Iodide of Potassium	1½ „

The exact quantity of soluble cotton which will be required cannot be stated with precision, since some samples produce a far more glutinous solution than others. The rule to be followed is to keep the texture of the film as slight as possible, since with so small an amount of Iodide a great improvement in the definition and sharpness of the image is produced in that way. If the quantity specified yields a solution fluid like water, and running down the neck of the bottle in the attempt to pour it on the plate, it may be increased.

The quantity of Iodide of Potassium must be regulated by the *appearance of the film* after dipping in the Bath.* It should be a pale blue, and very transparent; if the room is dimly illuminated, the film will scarcely be seen distinctly, and must therefore, after washing, be brought out to the light for inspection.

It is necessary that the Ether and Alcohol in this Collodion should be unusually pure, or it will be impossible to work with such a film. The purity of the materials may usually be measured by the rapidity of coloration on iodizing the Collodion. If (when iodized with Iodide of Potassium) it begins to change visibly in two or three minutes, and attains to a yellow colour in a quarter of an hour, the probability is that the half tones of the result-

* The Author invariably employs Iodide of Ammonium (prepared according to the method described at page 223), in preference to any other Iodide, for iodizing Collodion. Although at the time of mixing the ingredients (see page 97) the result is the same with the Iodides of Potassium, Ammonium, or Cadmium, yet after the expiration of a few hours, a minute amount of decomposition takes place in the two former cases, which at that early stage is favourable to sensitiveness. Hence if the Collodions be tested again on the following day, the Ammonium Salt has the advantage, both that and the Potassium being superior to the Cadmium. At the expiration of some weeks however, the decomposition increasing still further, the order of things is exactly reversed;—the Collodion iodized with Cadmium stands then at the head of the list, and that with the Ammonium last. These experiments were made with Ether originally purified from Alkali, but which had acquired a very slight amount of the colouring principle by keeping.

ing Positive will be inferior. In that case a very fair result may still be obtained by adding more Iodide, to enable the film to stand the retarding effects of the impurity. Indeed, by proper management in this particular, the operator will seldom be liable to disappointment, even although the quantities of ingredients laid down should be found to be too small.

The indication for *reducing* the amount of Alkaline Iodide is—excess of intensity in the high lights, combined with good half-tones and sensitiveness of Collodion. The Author has obtained pictures with soluble cotton and Iodide, each one grain, but has not been able to carry the reduction beyond that point.

With regard to the length of time this Collodion can be kept in working order, everything will depend upon the condition of the Ether. If recently distilled, probably the colour will scarcely have passed the lemon-yellow stage at the expiration of a fortnight, or even with Iodide of Potassium three weeks or a month. This lemon-yellow does no injury to the most delicate film, but when the colour reaches to a decided brown, the Iodine must be removed (see page 101).

In place of the Iodide of Potassium given in the formula, *the Iodide of Cadmium* may be substituted. In that case no coloration takes place; but this must not be taken to imply that an impure sample of Ether containing acid may be used.

The Writer does not from experience advise to keep a stock of the dilute Collodion *uniodized* for more than a month or six weeks; the tendency to decomposition in the Ether seems to be increased slightly by the solution of the Pyroxyline.

Modification of the formula adapted for commercial Ether and Alcohol.—If the pure spirits cannot be obtained, very good Positives are produced by slightly modifying the formula.

Rectified Ether	6 drachms
Spirits of Wine	2 „
Soluble Cotton	2½ grains
Iodide of Potassium . . .	2½ „

This film should be opalescent, and tolerably transparent.

B. THE NITRATE BATH.

Nitrate of Silver, crystallized *and dried*, but not fused	21 grains.
Distilled water	1 ounce.

Saturate with Iodide and Carbonate of Silver, according to directions given at page 226. Then add a standard solution of Nitric Acid (see page 229) until the faintly alkaline condition is removed, and no fogging takes place under the influence of the developer. The quantity of standard acid required to effect this in a ten-ounce Bath will probably be about three or four drops.

The proportion of Nitrate of Silver recommended in this Bath is unusually small; but the writer finds that with a pale film the image is better under such circumstances. Independently of other considerations, an excess of development is more to be feared with a strong than with a weak Bath.

If the film is used somewhat thicker than that recommended, and especially if large bluish patches of non-development occur, there can be no objection to increasing the proportion of Nitrate of Silver from 20 to 25 grains to the ounce; but in that case the developing solution must be proportionally weakened.

Although the Nitrate Bath may be perfectly neutral when first prepared, it becomes *distinctly acid* after a certain number of plates, perhaps forty or fifty, have been immersed; therefore if any deterioration of half tones is perceived, leading to a suspicion of free Nitric Acid, a

drop or two of the standard alkaline solution must be added until the evil is removed.*

With regard to the exact length of time such a Bath will remain in working order, no positive opinion can be given. If the solution is carefully guarded from the light, there is no reason to suppose that any decomposition of consequence would ensue; but the films are excessively delicate, and the proportion of the Silver salt being small, the expense of renewal is considerably lessened.

The addition of *Alcohol* to the Nitrate solution is not recommended. The Collodion already contains sufficient for the purpose.

Modification by which the difficulty of preserving the Bath accurately neutral is avoided.—If a small portion of *Acetate* of Silver be added to the Bath (see page 227), it will not be necessary afterwards to take the same pains in preserving the solution chemically neutral. The Acetate of Silver substitutes free Acetic Acid for Nitric, and a minute quantity of Acetic Acid does no injury. It is possible however that the operator may find a difficulty in preserving the pureness of the white in the parts most exposed to light, if any easily reducible salt of Silver is added to the Bath. (See page 146.)

C. THE DEVELOPING FLUID.

Protosulphate of Iron, pure and crystallized	12 to 16 grains.
Glacial Acetic Acid	8 to 12 minims.
Alcohol	10 minims.
Distilled water	1 ounce.

From the varying proportion of *Per*sulphate in the Proto-

* The fact of so little free Nitric Acid producing injurious effects, is explained by the delicate structure of the transparent Iodide films, and the small proportion of Nitrate of Silver in the Bath. (See page 132.)

sulphate of Iron of commerce, the number of grains to be used cannot be given nearer than above.

The Alcohol is added for the purpose of causing the solution to flow more easily, but it appears also to modify the tint slightly.

The Acetic Acid renders the development uniform, by causing the solution of Protosulphate to combine more readily with the film; also, with the Protosulphate used alone, without acid, the *colour* of the image is different in certain parts of the plate, varying from grey to white.

The rule to be followed is—to employ the solution of Protosulphate as concentrated as can be done without the occurrence of curved lines of over-development. With a weaker developer the image is equally white whilst wet, but becomes slightly metallic on drying.

The employment of a *Bath* of Sulphate of Iron is not recommended for neutral films; neither is *redipping* in the Nitrate solution after removal from the Camera. Both of these expedients, although safe in the ordinary way, are apt to produce foggy pictures with the most transparent films.

If glacial Acetic Acid is not at hand, Sulphuric Acid, ½ minim, may be used instead; the addition of much mineral acid to the developer, however, injures the image in the case of a twenty-grain Bath and neutral films. For the same reason the *Nitrate* of Iron cannot be substituted for the Sulphate; it refuses to develope with so small a proportion of Nitrate of Silver.

Pyrogallic Acid with Nitric succeeds to a certain extent, but it is inferior to the Iron Salt, and often causes green and blue patches of non-development, unless the strength of the Nitrate Bath be increased.

The image produced by the formula, as above given, is of a dead white, with absence of metallic lustre.

The solution of Sulphate of Iron may be preserved for

a long time; but it becomes peroxidized slowly, and consequently weaker, for which allowance must be made by fresh addition of the salt.

D. THE FIXING SOLUTION.

Cyanide of Potassium	1 or 2 grains
Water	1 ounce.

Cyanide of Potassium is superior to the Hyposulphite of Soda for fixing Positive impressions: it is less liable to injure the purity of the white colour.

Commercial Cyanide of Potassium always contains a large percentage of Carbonate of Potash; so that no exact directions can be given for the formula. It is well however to use it *as dilute as possible*—of such a strength that the plate is cleared gradually in from half a minute to a minute. (See page 56.)

The solution of Cyanide of Potassium decomposes slowly on keeping, but it will usually last for several weeks.

THE ORDINARY DIRECT POSITIVE PROCESS.

A. THE COLLODION.

This is the same as that recommended for Negatives in the next Section (page 245). If the film is dense, and the Bath only slightly acid from Acetic Acid, very probably the high lights will act too violently. In that case, supposing it not to be desirable to interfere with the Bath, add a few drops of Alcoholic solution of Iodine, until the Collodion assumes an orange tint; or introduce a red-hot wire for a short time into the upper part of the bottle, which will have the same effect. (See page 100.)

B. THE NITRATE BATH.

The Negative Bath given in the next Section (page 246) may be used. But if a new one is prepared purposely for

Positives, omit the addition of Acetate of Silver, and increase the amount of Acetic Acid somewhat, unless the Collodion is brown from free Iodine.

C. THE DEVELOPING FLUIDS.

Either of the three following formulæ may be used, according to the taste of the operator.

FORMULA No. 1.

Sulphate of Iron	20 grains.
Nitric Acid	½ minim.
Acetic Acid (glacial)	20 minims.
Alcohol	10 minims.
Water	1 ounce.

FORMULA No. 2.

Pyrogallic Acid	2 grains.
Nitric Acid	1 drop.
Water	1 ounce.

FORMULA No. 3.

Solution of Protonitrate of Iron	1 ounce.
Alcohol	20 minims.

In all these formulæ, if distilled water is not at hand, clean rain-water will answer the purpose, or pump-water which has been boiled to separate Carbonate of Lime. If the addition of a few drops of Nitrate of Silver however produces *a decided precipitate*, indicating the presence of soluble Chlorides in considerable quantity, the water is too impure for the purpose. Before testing, acidify with Nitric Acid, in order to prevent the *Carbonate of Silver* from being deposited as well as Chloride.

Miscellaneous Remarks upon these Formulæ.—Formula No. 1 is the most simple of all, since it can be used *as a*

Bath, the same portion being employed many times successively. If it acts too rapidly, lessen the proportion of Sulphate of Iron. An increase in the Nitric Acid makes the image whiter and more metallic; but if too much is added, the development proceeds irregularly, and spangles of Silver are formed.

After the solution has been some time in use, it becomes red from gradual formation of *per*salt. When it is too weak, add more of the Protosulphate. The muddy deposit which settles to the bottom of the Bath is metallic Silver, reduced from the soluble Nitrate upon the plates.

Formula No. 2 is employed when the amateur objects to the sparkling metallic pictures produced by the Iron Salts in conjunction with Nitric Acid. If the colour of the image is not sufficiently white, try the effects of increasing the amount of Nitric Acid slightly. On the other hand, if the development is imperfect in parts, and patches of a green colour are seen, use *three grains* of Pyrogallic Acid in place of two, with less Nitric Acid. Supposing this not to succeed, a few drops of Nitrate of Silver solution added to the Pyrogallic, immediately before use, will augment the energy of development.

Formula No. 3, or Protonitrate of Iron, does not require any addition of Nitric Acid; but it will be advisable, in some cases, to add to it a few drops of Nitrate of Silver immediately before developing. It gives excellent results, perhaps better than the Sulphate of Iron, if the trouble of preparing it is not objected to.

D. THE FIXING SOLUTION.

The Cyanide of Potassium may be used, but the solution should be somewhat stronger than that recommended at page 238, the film of Iodide of Silver being considerably more dense. A *Bath of Cyanide* may conveniently be employed in preference to pouring on the solution, but it de-

composes rapidly, unless the plates are well washed before fixing, in order to remove the whole of the Salts of Iron.

E. THE WHITENING SOLUTION.

Bichloride of Mercury . .	30 grains.
Distilled water	1 ounce.

By a gentle application of heat the corrosive sublimate entirely dissolves and forms a solution as nearly as possible *saturated* at common temperatures. The addition of a portion of Muriatic Acid enables the water to take up a far larger quantity of Bichloride; but this concentrated solution, at the same time that it whitens more quickly than the other, is apt to act unequally upon different parts of the image.

Before applying the Bichloride, the image is to be fixed and the plate well washed. Either the Protosulphate of Iron or the Pyrogallic Acid with Acetic may be used for the development; but the whitening process is more rapid and uniform in the latter case, the metallic particles being more finely divided.

GENERAL REMARKS ON THE POSITIVE PROCESSES ABOVE GIVEN.

The amateur is recommended to commence by taking direct Positive pictures in preference to Negatives, and at first to employ a *tolerably highly Iodized Collodion*, in conjunction with *an Acid Bath*, or in place of that, with addition of free Iodine. By this means he will obtain a film, which, although somewhat wanting in sensitiveness, will be a serviceable one, and very little prone either to *stains* or *fogging*. Afterwards, when he has mastered the manipulation, and especially if he is able to obtain chemicals which can be depended upon for purity, he may proceed to try some of the more sensitive processes, either by

addition of accelerating agents to the Collodion, or by the use of neutral films.

As far as landscapes and all objects of still life are concerned, time of exposure is of little moment, but with objects liable to move, it is well to reduce it to a minimum. The neutral transparent films are admirable in this respect, whilst at the same time they give an image very perfect in the shading, and with the faintest radiations perceptible.

Having determined on commencing a sensitive process, it is necessary that all the solutions should be prepared afresh, with adequate care, and especially that causes likely to produce fogging should be removed: the Bath must be tested for alkalinity—the developing room darkened with additional pains, and the Camera and slide rendered perfectly tight in every part. All the manipulatory details, with a few exceptions, must be performed rapidly, and especially the development of the image. The plates to be cleaned with extra precautions.

Lastly, observe this rule,—to guard the Nitrate Bath most carefully from all impurities, and especially from the action of light. If any decomposition takes place in it, everything will go wrong. The facility of reduction being increased, the developing fluids *will appear too strong*, acting with unusual violence, and producing fogging, stains, and spots of all kinds (see pp. 103 and 122). In that case the Bath is spoiled for neutral films, and can only be used with addition of acid.

SECTION II.

Formulæ, etc. for Negative Solutions.

As before, *two* processes will be given;—the first, a process of greater sensitiveness, adapted for Portraits; the second, the one ordinarily employed.

NEGATIVE PROCESS WITH NEUTRAL FILMS.

A. THE COLLODION.

Ether, washed and redistilled from alkali, sp. gr. ·720 . .	5 drachms.
Alcohol, rectified from Carbonate of Potash, sp. gr. ·825 . .	3 drachms.
Soluble Cotton.	2½ grains.
Iodide of Potassium	2½ grains.

For general remarks on this Collodion the operator is referred to the formula for dilute Positive Collodion, given in the last Section (page 232).

As before, the structure of the film is to be kept as slight as possible, in order to improve the definition of the image.

The appearance of the film of Collodio-Iodide of Silver produced by this formula should be of a silver-grey and comparatively translucent. The opalescent blue film produced by less Iodide succeeds tolerably well, but the shadows of the image are apt in that case to be misty and indistinct from fogging caused by the increased length of exposure required for a Negative.

On the other hand, if the quantity of Iodide be much increased, then the Nitrate Bath will scarcely be strong enough to cause a perfect decomposition.

B. THE NITRATE BATH.

This may be the same as that recommended in the first formula of the last Section; or the proportion of Nitrate of Silver may be increased from 20 to 25 grains to the ounce. Indeed, unless the structure of the film is slight, it will be necessary to do so in order to decompose the whole of the Iodide.

The author however prefers to keep the strength of the Nitrate Bath as low as possible, since experiments indicate

that a pale film of Iodide dipped in a very strong Bath, is somewhat less sensitive to half-tones than the same formed in a dilute Bath.

This point however, being of a delicate nature, is not asserted confidently; the operator must use his own judgment, always remembering that a certain definite quantity of metallic Silver is required to form the image, and that this amount must be added in the shape of Nitrate of Silver either to the Bath or to the developing fluid.

The addition of Acetate of Silver, in small proportion (about half the quantity recommended at page 246), admits of the Bath being used slightly acid, but care must be taken that the amount of even a weak acid, like Acetic, be not too far increased if sensitiveness is an object.

C. THE DEVELOPING FLUID.

Pyrogallic Acid	1½ grain.
Acetic Acid (glacial) . . .	5 minims.
Alcohol	15 minims.
Distilled water	1 ounce.

The development of the image is always more troublesome with neutral films, and the danger of stains greater than usual. Directions to avoid them are given in the next Chapter, on 'Manipulations.'

If the weather is cold and the development very slow, the quantity of Pyrogallic Acid may be increased even as far as three grains to the ounce. About 3 or 4 drops of the Bath solution added to each drachm of the developer, will furnish abundance of metallic Silver for the image.

NEGATIVE PROCESS WITH DENSE FILMS EMPLOYED FAINTLY ACID.

This is the ordinary Negative process, less sensitive than the last, but giving a very stable film, well adapted for

landscapes, etc. Excellent results can be obtained in this way, if the acidity is properly regulated, and kept proportionate to the density and structure of the film.

A. THE COLLODION.

Rectified Ether, sp. gr. ·750 . .	6½ drachms.
Alcohol, sp. gr. ·835	1½ drachm.
Soluble Cotton	4 grains.
Iodide of Potassium	5 grains.

The film produced by this Collodion should be tolerably dense, and more soluble cotton and Iodide must be added if it is not so.

If the Collodion is glutinous, and produces a wavy surface, it is probable (unless the Alcohol employed were inferior) that the Pyroxyline is in fault. In that case, try Mr. Shadbolt's formula of adding Chloroform ten drops to each ounce of the fluid.

On the other hand, if the Collodion is limpid, it will be likely to bear the addition of more Alcohol, and if so, an increase of sensibility may be obtained in that way. The proportion of spirit however is not to be increased beyond two drachms to the ounce, as the Ether already contains a certain portion of Alcohol.

If the film is decidedly creamy and opaque, the Ether good, and the Bath containing no free Nitric Acid, a somewhat better result, as far as half-tones are concerned, will be obtained by diminishing its thickness.

If *flakes of Iodide of Silver* are seen loose upon the surface of the film, and falling away into the Bath, the Collodion is over-iodized, and it will be impossible to obtain a good picture.

After the Collodion has been employed to coat a number of plates, the relative proportions of Alcohol and Ether contained in it become changed, from the superior

volatility of the latter fluid. Therefore, when it ceases to flow readily, and gives a more dense film than usual, thin it down by addition of a little rectified Ether.

Most operators adopt the plan of keeping on hand a stock of the plain Collodion, and iodizing as required by the addition of alcoholic solution of Iodide of Potassium. The plain Collodion however does not keep well beyond a certain length of time without a considerable development of the acid principle. (See page 100.)

In dissolving the Pyroxyline, any fibrous or flocculent matter which resists the action of the Ether, must be allowed to subside, the clear portion being decanted for use. The Iodide of Potassium is to be *finely powdered*, and digested with the spirit for several days, if a saturated solution is required; it is better not to apply any heat. Both Iodide of Ammonium and Iodide of Cadmium should dissolve almost immediately, if the salts are pure.

When this Collodion becomes very highly coloured, a part of the free Iodine may be removed by a strip of pure zinc or silver foil; also the metallic powder obtained by reducing Nitrate of Silver with Sulphate of Iron, acidified with Nitric Acid, answers well for the same purpose.

However, as long as the film continues to yield good Negatives, it is better to allow the Iodine to remain, even although the colour reaches to a decided brown.

B. THE NITRATE BATH.

Nitrate of Silver, crystallized and dried	36 grains.
Alcohol	10 minims.
Acetate of Silver	¼ grain.
Acetic Acid (glacial)	½ minim.
Distilled water	1 ounce.

This Bath is first to be saturated with Iodide and Carbonate of Silver, according to the directions given at page 225, and the Alcohol, Acetate of Silver, and Acetic Acid

are to be added subsequently. If the *Acetate of Silver* cannot be procured, the Acetate of Soda, prepared according to the directions given at page 227, will succeed equally well.

Rain-water may be used in place of distilled water, or *common water* which has been boiled to precipitate Carbonate of Lime. Even the presence of Carbonate of Lime however would not interfere. It would serve in part to neutralize any excess of Nitric Acid; or, if the solution was already neutral, would be precipitated as Carbonate of Silver.

After a large number of plates have been dipped, the Acetate of Silver becomes by degrees converted entirely into *Nitrate* (see p. 153), and the quantity of *free Acetic Acid* is increased. By adding a grain or two of crystals of Carbonate of Soda, the original condition is restored.

If a Nitrate Bath, prepared as above described, is carefully shielded from the light, it will remain in working order for many months. The proportion of Nitrate of Silver becomes, after a time, somewhat less, but not to the extent that might *à priori* be imagined.

However, it may be well occasionally to test it according to the method given in Part III., and to supply any waste which is found to have occurred.

C. THE DEVELOPING SOLUTION.

Pyrogallic Acid	1 grain.
Acetic Acid (glacial) . . .	8 minims.
Alcohol	10 minims.
Distilled water	1 ounce.

If the image cannot be rendered sufficiently black, two drops of the Nitrate Bath solution may be added to each drachm of the developer.

Also the proportion of Pyrogallic Acid may, if required, be increased.

If the solution be kept for some time after its first preparation, it is apt to become brown and discoloured. In order to avoid this, it has been recommended to make it about four times more concentrated than is necessary, and to dilute down with distilled water when required for use.

D. THE FIXING LIQUID.

Cyanide of Potassium .	2 to 10 grains.
Water	1 ounce.
or, Hyposulphite of Soda .	½ ounce.
Water	1 „

Cyanide of Potassium is preferable, in some respects, to the Hyposulphite of Soda for fixing Negatives; the glasses are more readily cleaned, and the films easier washed. Many however have been deterred from using the Cyanide by the solvent action which it exerts on the image, if employed in too concentrated a state. This is especially seen with Pyrogallic Acid as a developer, the particles of metallic Silver being, in that case, more finely divided. For further remarks, see the last Section, page 238.

CHAPTER III.

MANIPULATIONS OF THE COLLODION PROCESS.

THESE may be classed under five heads :—A. Cleaning the Plates.—B. Coating with Collodio-Iodide of Silver.—C. Exposure in the Camera.—D. Developing the image.—E. Fixing the image.

A. CLEANING THE PLATES.

Much care should be taken in the selection of glass intended to be used for Photographic purposes. The ordinary window-glass is often inferior, having scratches upon the surface, each of which causes an irregular action of the developing fluid. Also the squares are seldom perfectly flat, so that they do not touch the slide at every point, and hence a part of the image is out of focus. A more serious inconvenience, arising from want of flatness, is, that the plates are apt to be broken in compression during the printing process.

The patent plate answers perhaps better than any other description of glass, and it can be procured in small squares at a price not more than double that of the ordinary crown glass.

Before proceeding to the washing of the glasses, each square should be roughened on the edges by means of a file or a sheet of emery-paper. If this precaution is omit-

ted, not only are the fingers liable to injury, but the Collodion film is apt to contract and separate from the sides.

In the process of cleaning the glasses, it is not sufficient —as a general rule—to wash them simply with water; other liquids are required to remove *grease*, if any is present. For this purpose perhaps Caustic Potash, sold in druggists' shops under the name of "Liquor Potassæ," is as good as any, or if that is not at hand, a warm solution of the common washing Soda—which is a Carbonate. The Potash however is the better of the two.

Liquor Potassæ, being a very caustic and alkaline liquid, requires care in the handling; it softens the skin, and dissolves it away even more so than acids. A safe plan of proceeding is to dilute the Potash with about four parts of water, and to apply it to the glass by means of a cylindrical roll of flannel; after wetting both sides of the glass thoroughly, allow it to stand for a time until several have been treated in the same way; afterwards wash well with water and rub dry in a cloth.

The cloths used for cleaning glasses should be kept expressly for that purpose; they are best made of a material sold as "fine diaper," and very free from flocculi and loosely adhering fibres. They are not to be washed *in soap and water*, but always in pure water or in water containing a little Carbonate of Soda.

After wiping the glass carefully, complete the process by polishing with an old silk handkerchief, avoiding contact with the skin of the hand. Some object to *silk*, as tending to render the glass electrical, and so to attract particles of dust, but in practice no inconvenience will be experienced from this source.

Before deciding that the glass is perfectly clean, never omit to hold it in an angular position and to *breathe* upon it; many stains will be rendered visible in that way which could not otherwise have been seen.

The use of an alkaline solution is usually sufficient of itself to clean the glass, but occasionally we meet with plates dotted on the surface with small white specks, which are not removed by the Potash. These specks consist frequently of hard particles of *the Carbonate of Lime*, and when that is the case they dissolve very readily in dilute acid. Oil of Vitriol, with about four parts of water added, applied by means of a roll of flannel, answers well: so also does dilute Nitric Acid.

The objection to the use of Nitric Acid is, that if it is allowed to come in contact with the dress, it produces stains which cannot be removed *unless immediately treated with an alkali.*

Some operators employ the Cyanide of Potassium, and others Ammonia, in cleaning the plates; neither however possesses any advantage over the Liquor Potassæ.

In cases where Positives are to be taken, it is advisable to use additional care in preparing the glass, *and especially so with the opalescent films employed neutral.* The operator will find under such circumstances that *transparent lines and markings* are common enough, unless he is very careful.

After a glass has been once coated with Collodion, it is not necessary in cleaning it a second time to use anything but pure water; but if the film has been allowed to harden and to dry upon the glass, possibly the dilute Oil of Vitriol may be required to remove stains.

If under similar circumstances a greasiness is perceived, which prevents the plate from being wetted evenly by a stream of water poured upon it, this may be removed by a second application of the alkaline liquid.

B. COATING THE PLATE WITH THE COLLODIO-IODIDE OF SILVER.

This part of the process, as well as that which follows,

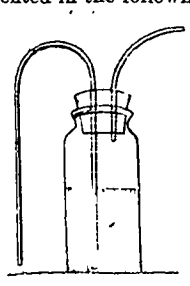
must be conducted in a room from which chemical rays of light are excluded. It is inferred therefore that the operator has provided himself with an apartment of that kind.

The most simple plan of darkening a room is to nail a double thickness of yellow calico completely over the window, and this will generally be found sufficient to prevent fogging with films of ordinary sensibility.

With the transparent neutral films, however, the writer always finds it better to illuminate by means of a lamp or candle screened by yellow glass. A dark orange yellow, approaching to brown, is more impervious to chemical rays than a lighter canary yellow. Of course the more sensitive the plate the greater the tendency to fogging, and hence it often happens that a room which has long been used successfully with acid films, is found to fail with the neutral films.

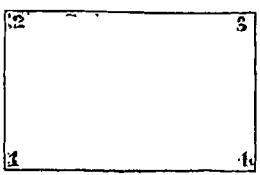
Before coating the plate with the Collodion it may be well to examine that it is perfectly clear and transparent, and that all particles of dust, etc., have settled to the bottom; also that the neck of the bottle is free from hard and dry *crusts*, which, if allowed to remain, would partially dissolve and produce striæ upon the film.

A very useful little piece of apparatus for clearing Collodion is that represented in the following woodcut.



The Collodion, having been iodized some hours previously, is allowed to settle down and become clear in this bottle; then by gently blowing at the point of the shorter tube, the small glass siphon is filled and the fluid drawn off more closely than could be done by simply pouring from one bottle to another.

When the Collodion is properly cleared from sediment of every kind, the operator takes a glass plate, previously cleaned, and wipes it gently with a silk handkerchief, in order to remove any particles of dust which may have subsequently collected. If it be a plate of moderate size, it may be held by the corners in a horizontal position, between the fore-finger and thumb of the left hand. The Collodion is to be poured on steadily until a circular pool is formed, extending nearly to the edges of the glass,



By a slight inclination of the plate the fluid is made to flow towards the corner marked 1, in the above diagram, until it nearly touches the thumb by which the glass is held; from corner 1 it is passed to corner 2, held by the forefinger; from 2 to 3, and lastly, the excess poured back into the bottle from the corner marked No. 4. It is then to be held vertically over the bottle for a moment, until it nearly ceases to drip, and then, by raising the thumb a little, the direction of the plate is changed, so as to cause the diagonal lines to coalesce and produce a smooth surface. The operation of coating a plate with Collodion must not be done hurriedly, and nothing is re-

quired to ensure success but steadiness of hand and a sufficiency of the fluid poured in the first instance upon the plate.

Length of time to be allowed to elapse before immersing in the Bath.—The only criterion is the appearance of the film after its removal from the Bath. This has been sufficiently described at page 109, to which the operator is therefore referred. The following general directions however may be of service. With the sensitive dilute Collodion for direct Positives allow five seconds, if the weather is mild; but if the temperature is unusually high, immerse the plate almost immediately. The ordinary Negative Collodion may perhaps require about twenty seconds in the common way, or ten seconds in hot weather. When the operator has once seen the *peculiar reticulated appearance* and the transparent cracks upon the lower edge of the film, characteristic of a too rapid immersion, he will require no other guide for the future.

The proper time having elapsed, rest the plate upon the glass dipper, Collodion side uppermost, and lower it into the solution by one steady movement: if any pause is made, a horizontal line corresponding to the surface of the liquid will certainly be formed; then place the cover upon the vertical trough and darken the room, if this has not already been done. As the presence of white light does no injury to the plate previous to its immersion in the Bath, it is not necessary altogether to exclude it during the time of coating with Collodion.

When the plate has remained in the solution from thirty seconds to a minute, lift it partially out two or three times, in order to wash away the Ether from the surface. About three minutes' immersion will usually be sufficient, or five minutes in cold weather, and with Collodion containing but little Alcohol. When the oily streaks upon the surface disappear, and the liquid flows off in a uni-

form sheet, the decomposition may be considered to be perfect.

The plate is then removed from the dipper, and held vertically in the hand for a few seconds, to drain off as much as possible of the solution of Nitrate of Silver. It is then placed in the slide, Collodion side downwards, and is ready for the Camera.

At page 109, already referred to, the student is strongly recommended not to proceed to the actual process of taking pictures in the Camera until by a little practice he has succeeded in producing a perfect film, which is uniform in every part, and will bear inspection when washed and brought out to the light.

C. EXPOSURE OF THE PLATE IN THE CAMERA.

The operator is supposed, before arriving thus far, to have ascertained that the joints of the Camera are tight in every part,—that the sensitive plate, when placed in the slide, falls precisely in the same plane as that occupied by the ground glass,—and that the chemical and visual foci of the Lens accurately correspond.*

It is best to commence by focussing some object near at hand,—at all events, if the full aperture of a double combination Lens is employed. The powerful light reflected from landscape scenery, etc., would probably confuse the beginner by producing fogging of the plate.

Therefore, taking the case of a portrait, proceed to arrange the sitter as nearly as possible in a vertical position, in order that every part may be equidistant from the lens. Then, supposing an imaginary line to be drawn from the head to the knee, point the Camera slightly downwards, so that it may stand at right angles to this line. The

* The points here mentioned are of such importance that directions with regard to them will be given at the end of this chapter (page 263).

distortion of the image, so often complained of, is thus avoided to a considerable extent.

A background of a dark or middle tint, and of such a size as to completely cover the field of the Camera, is placed behind the sitter. If the open sky, or any other distant object, brightly illuminated, were used to form a background, the probability is, that with the full aperture of the lens, fogging would be produced from over-exposure.

In order to succeed well with portraits, it is also necessary that the sitter should be well illuminated by an even diffused light falling horizontally. A vertical light causes a deep shadow on the eyes, and therefore it must be cut off by a curtain of blue calico suspended over the head. The direct rays of the sun are to be avoided, as causing too great a contrast of light and shade. In particular, *the Lens* is to be shielded from the sun's rays, or the pictures will be misty from diffused light. By a simple arrangement of curtains, it is easy to alter the direction of rays of light, so that one half of the sitter may be more brightly illuminated than the other, by which a better effect is obtained. In focussing the object, cover the head, and back part of the Camera, with a black cloth, and shift the lens gently until the greatest possible amount of distinctness is obtained.

Exposure of the plate.—The amateur will naturally desire to have very explicit directions on this head; but so much depends upon the brightness of the light and the nature of the Collódion, that the proper time for exposure must be left almost entirely to experience. The following general rules may however be of use.

In a tolerably bright day in the spring or summer months, and with the Collodion given at page 245, allow three seconds for a positive portrait, and eight seconds for a negative. With a double-combination Lens of large

aperture and short focus, perhaps two seconds, and six seconds, or even less, may be sufficient.

The sensitive Collodion of pages 232 and 243 will yield a positive in one to three seconds, and a negative in three to six seconds.

In the dull winter months, multiply these numbers about four times, which will be an approximation to the exposure required. It is by the appearance presented under the influence of the developer, which will immediately be described, that the operator ascertains the proper time for exposure to light.

D. THE DEVELOPMENT OF THE IMAGE.

The details of developing the latent image differ so much in the case of Positive and Negative pictures, that it is better to describe the two separately.

a. *The development of direct Positives.*—With the ordinary Collodion of page 245, and Sulphate of Iron as a developer, it is more simple to develope the image by immersion. Therefore the solution may conveniently be poured into a vertical trough, such as that used for exciting, and the plate immersed by means of a glass dipper in the usual way. Unless the weather is cold, the image makes its appearance in a few seconds, and the film is then immediately washed with clear water. Whilst in the Bath, the plate is kept in gentle motion, and the operator must not expect to see the image very distinctly, except the high lights; the shadows, being faint, are partially concealed by the unaltered Iodide, but they come out during the fixing. The action of the Sulphate of Iron is stopped at an early period, or an excess of development will be incurred.

In using Pyrogallic Acid or Nitrate of Iron to develope glass Positives, the plate may be placed upon a levelling-

stand, or held in the hand, and the solution poured on quickly at one corner; by blowing gently or inclining the hand, as the case may be, it is scattered evenly over the film before the development commences.

Development of the transparent Neutral films.—The writer has not been successful in the use of a Bath with these films. The plates are spotted and slightly fogged if the same portion of developer is employed more than once. It is always a matter of some little difficulty to cover a plate evenly with a strong solution of Sulphate of Iron before the action commences; with a little practice however it may be done, by using a shallow *cell* formed from two or three thicknesses of window-glass, cemented on a piece of patent plate to the depth of a quarter of an inch. The size of the cell should be only slightly larger than the plate intended to be developed, that the waste of fluid may be as little as possible.

This cell is held in the left hand, and the plate being placed in it, a sufficient quantity of the developer is poured on at one corner. By a slight inclination, the fluid is caused to flow in a uniform sheet over the surface of the film, backwards and forwards. The image starts out almost instantaneously, and the developer is then at once poured off, and the film washed as before.

It is very important in developing neutral films to use a sufficient quantity of the solution to cover the plate easily; otherwise, oily stains and marks are formed from the developer not combining properly with the surface of the film. For a plate five inches by four, five drachms will be required, and so in proportion for larger sizes.

The time occupied in developing will seldom be more than a few seconds, the shading being injured by carrying the process too far.

The appearance of the image after developing, as a guide to the proper time of exposure.—When the plate has

been developed, it is washed, fixed, and laid upon a dark ground, such as a piece of black velvet, for inspection.

In the case of a portrait, if the features have an unnaturally black and gloomy appearance, the dark portions of the drapery, etc. being invisible, the picture has been *under-exposed*.

On the other hand, in an over-exposed plate, the face is usually pale and white, and the drapery misty and indistinct. Much however in this respect depends upon the dress of the sitter (see p. 196), and upon the manner in which the light is thrown; if the upper part of the figure is shaded too much, the face may perhaps be the last to be seen. The operator should accustom himself to expend much pains in the preliminary focussing upon the ground glass, and to ascertain at that time that every part of the object is equally illuminated. For this reason, pictures taken in a room are seldom successful; the light falls entirely upon one side, and hence the shadows are dark and indistinct.

b. *The development of Negative pictures.*—This process differs in most respects from that of Positives. In the latter case, there is a tendency to over-develope the image; but in the former, to stop the action at too early a period, hence it is common to find Negative pictures which are insufficiently developed and too pale to print well.

In the development of Negatives, many operators place the plate upon a levelling-stand, and distribute the fluid by blowing gently upon the surface; others prefer holding it in the hand and pouring the fluid on and off from a glass measure.

The flat cell of glass already described is useful when any difficulty is experienced in covering the plate before the action begins.

With the ordinary Negative Collodion of page 245, the addition of Nitrate of Silver to the developer may not be

required; at all events, the Pyrogallic Acid is to be used alone until the image has reached its maximum of intensity, which it will usually do in a minute or so, according to the temperature of the developing room. The plate may then be examined leisurely by placing it in front of, and at some distance from, a sheet of white paper. If it is not sufficiently black, add about two drops of the Nitrate Bath to each drachm of developer, stir well with a glass rod, and continue the action until the requisite amount of intensity is obtained.

The development of the neutral films produced by the sensitive Collodion of page 243, differs in no important particular from the others, but there is a greater tendency than usual to stains and spots. In very cold weather the Pyrogallic Acid may be mixed with a portion of the Bath solution (five drops to the drachm), before pouring it on the plate.

Appearance of the image during and after the reducing process, as a guide to the exposure to light.—An under-exposed plate developes slowly. By continuing the action of the Pyrogallic Acid, the high lights become very black, but the shadows are still invisible, nothing but the yellow Iodide being seen on those portions of the plate. After treatment with the Cyanide, the picture shows well as a Positive, but by transmitted light all the minor details are invisible; the image is black and white, without any half-tone or sharpness of outline. In such a case, the development may have been conducted properly, but the time of exposure in the Camera was insufficient.

An over-exposed Negative developes rapidly at first, but soon begins to blacken slightly at every part of the plate. After the fixing is completed, nothing can be seen by reflected light but a uniform grey surface of metallic Silver, without any appearance (or, at most, an indistinct one) of an image. By transmitted light the plate appears of a

blood-red colour (if Acetate of Silver is present in any quantity in the Bath), and the image is faint and dull. The clear parts of the Negative being obscured by the fogging, and the half-shadows having acted so long as nearly to overtake the lights, there is a want of proper contrast; hence the over-exposed plate is, in this respect, the exact converse of the under-exposed, where the contrast between lights and shadows is too well marked from the absence of intermediate tints.

A Negative which has received the proper amount of exposure usually possesses the following general characters:—The image is almost but not quite invisible by reflected light. In the case of a portrait any dark portions of drapery show well as a Positive, but the features of the sitter are scarcely to be discerned. The plate has a general aspect as of fogging *about to commence*, but not actually established. By transmitted light the figure is bright and appears to stand out from the glass; the dark shadows are clear without any misty deposit of metallic Silver; the high lights black almost to complete opacity. The *colour* of the image however varies much with the state of the Bath, as has been already shown at page 153.

Negatives in which no image whatever can be seen by reflected light, often print fairly, but usually under those circumstances the deepest shadows of the resulting Positive are somewhat flat and indistinct (see page 186). A little consideration will show that if the whites of a Negative are slightly fogged, the blacks must be proportionably more intense than usual to produce the same effect.

The remarks already made under the head of Positives, apply equally well to Negatives; that is, it will be difficult to secure gradation of tone, unless the object is *equally* illuminated in every part, without any strong contrast of light and shade. Hence the direct rays of the sun are always to be avoided, and curtains, mirrors, etc. employed when practicable.

E. FIXING AND VARNISHING THE IMAGE.

After the development is completed, and the plate has been carefully washed by a stream of water, it may be brought out to the light and treated with the Hyposulphite, or Cyanide, until the unaltered Iodide is entirely cleared off. Some use a Bath for the Cyanide; but it is doubtful whether much saving is effected by doing so. The plate is again to be carefully washed after the fixing; and especially if Hyposulphite of Soda is used. Three or four minutes in running water will not be too long, or the glass may be left in a dish of water for an hour or two. If such precautions are neglected, crystals form on drying, and the picture is injured.

Lastly, stand the plate on end to drain, and when thoroughly dry protect it by a varnish. Dr. Diamond's formula, with Amber dissolved in Chloroform, succeeds well. It may be poured on the plate in the same manner as Collodion, and dries up speedily into a hard and transparent layer. The Spirit Varnish ordinarily sold for Negatives requires the aid of heat to prevent the gum from chilling as it dries;—the plate is first warmed gently and the varnish poured on and off in the usual way; it is then, whilst still dripping, held to the fire until the Spirit has evaporated. A few trials will render the operation easy to perform.

Direct Positives are to be varnished, first with a layer of transparent varnish, and then with black japan. Suggitt's patent jet is commonly employed, the only objection being its disagreeable smell. The transparent varnish should be tolerably white; but the yellow negative varnish dries into a colourless film if diluted down with an equal bulk of Alcohol. The black japan may be used alone; but in that case the Positives are slightly dull and wanting in brilliancy.

SIMPLE DIRECTIONS FOR FINDING THE EXACT CHEMICAL FOCUS OF AN ACHROMATIC LENS.

Non-Achromatic Lenses are understood by all to require correction for the chemical focus; but it is usually said of the compound glasses, that their two foci correspond. The amateur is recommended, by all means, in order to avoid disappointment, to test the accuracy of this statement, and also in addition to see that his Camera is constructed with care. To do this, proceed as follows:—

First, ascertain that the prepared sensitive plate falls precisely in the plane occupied by the ground glass. Suspend a newspaper or a small engraving at the distance of about three feet from the Camera, and focus the letters occupying the centre of the field; then insert the slide, with a square of *ground glass* substituted for the ordinary plate (the rough surface of the glass looking inwards), and observe if the letters are still distinct. In place of the ground glass, a transparent plate with a square of silver-paper which has been oiled or wetted, may be used, but the former is preferable.

If the result of this trial seems to show that the Camera is good, proceed to test the correctness of the Lens.

Take a Positive Photograph with the full aperture of the Lens, the central letters of the newspaper being carefully focussed as before. Then examine at what part of the plate the greatest amount of distinctness of outline is to be found. It will sometimes happen that whereas the exact centre was focussed visually, the letters on a spot midway between the centre and edge are the sharpest in the Photograph.* In that case the chemical focus is longer than the other, and by a distance equivalent to the space

* This observation applies only to the double combination Lens with full aperture. In the case of a single Lens and small diaphragm, the field would be flat and every part in good focus.

which the ground glass has to be moved, in order to define those particular letters sharply to the eye.

When the chemical focus is the shorter of the two, the letters in the Photograph are indistinct all over the plate; therefore the experiment must be repeated, the Lens being shifted an eighth of an inch or less. Indeed it will be proper to take many Photographs at minute variations of focal distance before the capabilities of the Lens will be fully shown.

CHAPTER IV.

CLASSIFICATION OF IMPERFECTIONS IN COLLODION PHOTOGRAPHS, WITH DIRECTIONS FOR THEIR REMOVAL.

SECTION I.—Imperfections common to both Negatives and Positives.
SECTION II.—Imperfections peculiar to Negatives.
SECTION III.—Imperfections peculiar to Positives.

SECTION I.

Imperfections common to Negatives and Positives.

The following may be mentioned:—fogging—specks—spots—markings of all kinds.

A. FOGGING OF COLLODION PLATES.

The theory of this subject has already been explained in the eighth Chapter of Part I., and the causes which produce it, ranged under two heads, viz. irregular action of light—and impurity of chemicals. The same division will still be adhered to.

IRREGULAR ACTION OF LIGHT AS A CAUSE OF FOGGING.

1. *Over-exposure of the Plate.*—This often happens from using the full aperture of a double combination Lens, in copying distant objects brightly illuminated, the Collo-

dion being highly sensitive. Also from the film containing too little Iodide of Silver. (See page 151.)

2. *Diffused Light in the developing Room.*—In proportion as the sensitiveness of the plates increases, greater care must be exercised in thoroughly excluding all rays of white light. With opalescent films, neutral, this cause of fogging is more common than any other.

3. *Diffused Light in the Camera.*—This may result from the slide not fitting accurately, or from the door not shutting quite close.

4. *Direct rays of the Sun falling upon the Lens.*

5. *Diffused Light of the Sky falling upon the Lens.*—With transparent neutral films and full aperture of a double combination Lens, a portion of sky included in the field (as, for instance, to form the background of a portrait) is apt to cause fogging.

IMPURITY OF CHEMICALS AS A CAUSE OF FOGGING.

1. *Use of fused Nitrate of Silver in preparing the Bath.*—Strongly fused Nitrate of Silver contains Oxide, and also Nitrite of Silver, both of which tend to produce fogging (page 136). As a remedy add Acetic Acid, one drop to the ounce of solution.

2. *Use of Collodion containing Ammonia or Carbonate of Ammonia.*—An alkaline Collodion may be used with advantage when the Bath contains free Nitric Acid, but in a neutral Bath it causes fogging (see page 105).

3. *Addition of any Alkali or Carbonate of an Alkali to the Bath.*—If either Potash, Ammonia, or Carbonate of Soda is added to the Nitrate Bath to remove Nitric Acid, it is necessary to test for "alkalinity" before using it again (page 106).

4. *Decomposition of the Bath by exposure to Light* (see page 103); *or by long keeping, even in the dark* (?).—The Author conceives that it is possible for organic matter

alone to produce, after a time, a partial decomposition of solution of Nitrate of Silver, sufficient to prevent it from being employed *chemically neutral*, but probably not much interfering with its properties in other respects.

5. *Omission of Acetic Acid in the solution of Pyrogallic Acid.*

6. *Introduction of a minute portion of Pyrogallic Acid into the Collodion.*—This may happen from using a dirty scale-pan in weighing out the Iodide.

The following causes of fogging may also be mentioned; but as of minor importance, and especially applying to the transparent neutral films, which from their exceeding delicacy require an unusual amount of care.

7. *Use of rain-water or of water containing Carbonate of Lime, for making a Bath, the Nitrate of Silver being perfectly neutral and free from Nitric Acid.*—This difficulty is not a theoretical one only, but has actually been experienced. Rain-water usually contains *Ammonia* and has a faint alkaline reaction. Pump-water often abounds with *Carbonate of Lime*, much of which, but not the whole, is deposited on boiling. To remove the alkaline condition add Acetic Acid, one drop to half a pint of the solution.

8. *Partial decomposition of the Bath by contact with metallic Iron—with Hyposulphite of Soda—or with any developing agent, even in small quantity.*—Also by the use of *accelerators*, which injure the Bath by degrees, and eventually prevent its employment in an accurately neutral state.

9. *Vapour of Ammonia, or Hydrosulphate of Ammonia, escaping into the developing room.*

10. *Development of the image by immersion.*—Developing direct Positives by immersion in a Bath of Sulphate of Iron is a simple plan when the film is acid, but with neutral films it is better to pour the fluid over the plate and not to use the same portion twice.

11. *Redipping the plate in the Bath before development.* —This, with the opalescent films, is apt to give a foggy picture, and especially so if a minute or two is not allowed for draining the plate after its second immersion.

SYSTEMATIC PLAN OF PROCEEDING IN ORDER TO DETECT THE CAUSE OF THE FOGGING.

If the amateur has had but little experience in the Collodion process, and is using Collodion of moderate sensitiveness and a new Bath, the probability is that the fogging is caused by *over-exposure.* Having obviated this, proceed to test the Bath; *if it does not restore the colour of reddened litmus-paper after one hour's immersion,* it may be depended upon as being in working order; nevertheless, in order to be quite sure, add sufficient Acetic Acid to give a faint acid reaction to test-paper.

Next prepare a sensitive plate, and immediately on its removal from the Bath, pour on the developer; after a few seconds, wash, fix, and bring out to the light; if any mistiness is perceptible, *the developing room is in fault.*

On the other hand, if the plate remains absolutely clear under these circumstances, *it is possible that the cause of error may be in the Camera;*—therefore prepare another sensitive film, place it in the Camera, and proceed exactly as if taking a picture, with the exception of not removing the brass cap of the Lens; allow to remain for two or three minutes, and then remove and develope as usual.

If no indication of the cause of the fogging is obtained in either of these ways, there is every reason to suppose that it is due to diffused Light gaining entrance through the Lens. (See the remarks at page 256.)

B. SPECKS UPON THE PLATE.

Opaque or transparent dots, thickly studding every part of the plate, are produced by the following causes:—

1. *The use of Collodion holding small particles in suspension:*—each particle becomes a centre of chemical action, and produces a speck, or what is technically termed 'a comet,' that is, a speck with a tail to it.

Collodion should never be employed immediately after mixing, but should be placed aside to settle for several hours, after which the upper portion may be poured off for use. This is especially necessary when the double Iodide of Potassium and Silver is employed; the salt is decomposed to a certain extent by *dilution*, and small particles of Iodide of Silver separate, which eventually settle to the bottom of the bottle. (See page 52.)

2. *Dust upon the surface of the glass at the time of pouring on the Collodion.*—Perfectly cleaned glasses, if set aside for a few minutes, acquire small particles of dust; each plate therefore should be gently wiped with a silk handkerchief immediately before being used.

3. *Employment of an inferior kind of glass, or of glass not cleaned with acid.*—The surface of the commoner descriptions of glass is oftentimes roughed and studded with minute specks; occasionally these can be removed by means of dilute acid, in which case they probably consist of Carbonate of Lime.

C. TRANSPARENT AND OPAQUE SPOTS.

Spots are of two kinds: spots of *opacity*, which appear *black* by transmitted light, and *white* by reflected light; and spots of *transparency*, the reverse of the others, being white when seen upon Negatives, and black on Positives.

OPAQUE SPOTS are referable to *an excess of development* at the point where the spot is seen; they may be caused by—

1. *The Nitrate solution being turbid.*—A. From flakes of Iodide of Silver having fallen away into the solution, by use of an over-iodized Collodion.—B. From a deposit

formed by degrees upon the sides of the gutta-percha trough.—C. From the inside of the trough being *dusty* at the time of pouring in the solution.

In order to obviate these inconveniences, it is well to make at least half as much again of the Nitrate solution as is necessary, and to keep it in a stock-bottle, from which the upper part may be poured off as it is required. The frequent filtration of Silver Baths is unadvisable, since the paper employed may be contaminated with impurities.

2. *From the developing fluid containing too much Nitric Acid.* (See page 274, Imperfections in Positives, No. 4.)

3. *Faults on the part of the Slide.*—Sometimes a small hole exists, which admits a pencil of light, and produces a spot, known by its being always in the same part of the plate; occasionally the door works too tightly, so that small particles of wood, etc. are scraped off, and projected against the plate when it is raised. Or perhaps the operator, after the exposure is finished, shuts down the door with a jerk, and so causes a *splash* in the liquid which has drained down and accumulated in the groove below; this cause, although not a common one, may sometimes occur.

SPOTS OF TRANSPARENCY are produced in a manner altogether different from the others. They may generally be traced to some cause *which renders the Iodide of Silver insensible to light at that particular point,* so that on the application of the developer no reduction takes place.

1. *Concentration of the Nitrate of Silver on the surface of the film by evaporation.*—When the film becomes too dry after removal from the Bath, the solvent power of the Nitrate increases so much that it is apt to eat away the Iodide and produce spots. (See page 102.)

2. *By raising the plate out of the Nitrate Bath too quickly after its first immersion.* (See next page, Stains on the Plate, No. 2.)

3. *By pouring on the developer entirely at one spot;* by which the Nitrate of Silver is washed away, and the development prevented. (See p. 274, Imperfections in Positives, No. 5.)

4. *By use of glasses improperly cleaned.*—This cause is perhaps the most frequent of all, when the opalescent neutral films are employed. (See page 251.)

D. MARKINGS OF VARIOUS KINDS.

1. *A reticulated appearance on the film after developing.*—When this is *universal,* it often depends upon the employment of Collodion of inferior quality. (See p. 96.) Or if not due to this cause, the plate may have been immersed too quickly in the Bath, and the soluble Cotton partially precipitated (page 108).

2. *Oily spots or lines* are often caused by raising the plate out of the Nitrate Bath before it has been immersed sufficiently long to have become thoroughly wetted. After doing so, the imbibition is unequal and the film imperfect. Another cause is the permanent removal of the plate from the Bath before the Ether upon the surface has been washed away. *A third*—redipping the plate in the Nitrate Bath after exposure to light, and pouring on the developer *immediately.* If a few minutes are not allowed to drain off the excess of Nitrate, the Pyrogallic Acid will not amalgamate readily with the surface of the film.

3. *Straight lines traversing the film horizontally,* caused by a check having been made in immersing the plate in the Nitrate Bath.

4. *Curved lines of over-development.*—By employing the developer too concentrated, or by not pouring it on sufficiently quickly to cover the surface before the action begins.

5. *Stains of varied appearance from too small a quantity of fluid having been employed to develope the image.*—In

this case, the whole plate not being thoroughly covered during the development, the action does not proceed with regularity.

5. *Irregular striæ*—from fragments of dried Collodion accumulating in the neck of the bottle, and being washed on the film; to avoid this, the finger should be passed gently round the inside of the neck before using.

6. *Markings resembling fern-leaves, etc. etc.*—The writer has frequently seen these in using a Bath which had acquired slight fogging propensities by decomposition. They are less injurious in the case of Negative than of Positive pictures. As a remedy, try the addition of Acetic Acid.

7. *Stains on the upper part of the plate from using a dirty slide.*—To avoid these, place, if necessary, strips of blotting-paper between the supports and the glass.

8. *Transparent lines and markings from imperfectly cleaned glasses.* (See page 251.)

SECTION II.

Imperfections peculiar to Negatives.

1. *The image is very distinct by transmitted light, and the shading good, but it is too pale to print well.*—In this case it is probable that the development was not pushed far enough; or that the film being somewhat transparent, the quantity of free Nitrate of Silver on the surface was insufficient. In that case add a few drops of the Bath, as already recommended. (See pages 119 and 260.)

2. *The image is very black in the high lights, but the shadows are not sufficiently marked; it shows well as a Positive.*—The picture is under-exposed (page 150), or the operator has not managed the light properly (page 259). The following causes may also produce the same appearance:—the Collodion prepared with a bad sample of

Ether (page 118); the Collodion over-iodized (page 107); *fused* Nitrate of Silver employed for the Bath (page 115); Iodide of Iron used as an accelerator, the Bath being strong and nearly neutral (page 133).

3. *The image is pale and misty by transmitted light, nothing can be seen by reflected light.*—The plate has been over-exposed (page 123), or there is diffused light in the Camera or in the developing-room (see page 266). Perhaps the film is too transparent for Negatives, or the Bath is alkaline.

4. *The image is intensely black and prints slowly; the Positives, when produced, are highly coppery in the darkest shadows.*—In this case it is probable that the Negative was under-exposed and over-developed.

5. *The high lights of the image are solarized.*—The term solarization is employed to denote so many different conditions, that it is difficult to use it with precision; but if a change of colour to a light brown or red tint is understood, this is favoured by the presence of easily reducible salts of Silver and of Oxide of Silver in the film (page 154).

SECTION III.

Imperfections peculiar to Positives.

The principal difficulty in the production of Negatives is to hit the right time of exposure to light and the proper point to which to carry the development of the image. A minor amount of fogging, stains, etc., is of less consequence, and will scarcely be noticed in the printing.

With direct Positives however the case is different. The beauty of these pictures depends entirely upon their being clean and brilliant, without fogging, specks, or imperfections of any kind. On the other hand, the exposure and development of Positives is comparatively simple and easily ascertained.

1. *The image shows well in the high lights, but the shadows are dark and heavy, and the whole picture has a sombre appearance.*—The plate has not received sufficient exposure in the Camera (page 142);—or it has been under-developed;—or one of the following causes is in operation.—The film is comparatively dense, and the Bath strong and nearly neutral (page 131).—The film being very transparent and the Nitrate solution weak, Nitric Acid is present in the Bath, or the Collodion is brown from free Iodine, or has been made with an impure sample of Ether (see pages 118 and 132).—The Collodion contains free Ammonia and gives a dense film, the Bath being nearly neutral (page 122).

2. *The shadows of the image are good, but the lights are overdone.*—The developing fluid may have been kept on too long; or some of the conditions mentioned immediately above may be present; or the object is not properly illuminated.

3. *The image is pale and flat in the high lights and misty in the shadows.*—The plate is over-exposed (page 142). The indistinctness of outline caused by over-exposure of a Positive is easily distinguished by its appearance from that produced by fogging.

4. *The image developes slowly, and is imperfect; spangles of metallic Silver are formed.*—Too much Nitric Acid is present in proportion to the strength of the Bath, to the amount of Iodide in the film, and to the quantity of Protosalt of Iron in the developer (pages 121, 145).

5. *Circular spots are seen which appear of a black colour after backing up with the varnish* (see p. 271, No. 2).—These are often caused by lifting the plate too quickly out of the Bath; or by pouring on the developer at one spot, so as to wash away the Nitrate of Silver; or by the use of glasses imperfectly cleaned (see page 251).

6. *The image, intended to be white and lustreless, be-*

comes metallic on drying.—If Sulphate of Iron was employed, the solution is too weak, or free Nitric or Sulphuric Acid has been added in excess.—If developed with Pyrogallic Acid the proportion of Nitric Acid is too great.

7. *The image has an unpleasant green tint in certain parts.*—If Pyrogallic Acid was used to develope, the quantity of Nitric Acid is probably too great in proportion to the strength of the Bath. Imperfect development from deficiency of Nitrate of Silver is generally characterized by a play of colours at the margin of the plate.

8. *The image is solarized in the high lights* (see page 146).

CHAPTER V.

THE PRACTICAL DETAILS OF PHOTOGRAPHIC PRINTING.

This Chapter may be divided into three Sections :—

SECTION I.—The preparation of the sensitive paper.

SECTION II.—Preparation of the fixing and colouring solutions.

SECTION III.—The general manipulatory details of the process.

SECTION I.

The Preparation of the Sensitive Paper.

In preparing Positive paper for Photographic purposes the process is divided into two parts ;—first, "salting" the paper, as it is termed, and second, rendering it sensitive. The salting is usually performed by preparing a considerable quantity of solution of Chloride of Sodium or Muriate of Ammonia, and floating the paper upon its surface, in a large flat dish, until a sufficient amount has been imbibed. Afterwards, in order to render it sensitive, a solution of Nitrate of Silver is *brushed* over the salted surface, or applied by floating in the same manner as before.

These operations may be described under the following heads :—A. The selection of a paper fitted for the purpose.

—B. The preparation of albumenized paper.—C. The preparation of Ammonio-Nitrate paper.

A. THE SELECTION OF THE PAPER.

Paper which is intended to be used in Photography should be selected with great care. There are several kinds manufactured purposely, and it is better on all occasions to use these in preference to the common varieties. A Photographic paper should be very smooth and uniform in texture; of equal thickness in every part. Also, it should be free from *spots*, which when present can be seen on holding the paper up to the light. These spots consist usually of small metallic particles, which, when the paper is rendered sensitive, act as centres of chemical action and spoil the effect.

There are two principal varieties of Photographic paper sold in commerce—the French and the English papers. The former are usually more porous than the latter, and are sized with starch. The English papers, on the other hand, are comparatively dense in structure and sized with gelatine.

The writer has had but little experience in the use of English papers, but they are said by many to require less strength of sensitizing solutions than the French. The reason may be that the latter, being more porous, absorb liquids very completely and leave less upon the surface.

The Positive paper of Canson Frères is a good paper, much recommended for albumenizing.

Of the English varieties those manufactured by Turner, and by Whatman, are found to succeed well.

B. PREPARATION OF ALBUMENIZED PAPER.

This is divided into—*a*, the salting and albumenizing,—*b*, the sensitizing with Nitrate of Silver.

a. *The salting and albumenizing.*—Take of

Chloride of Sodium or Ammonium .	40 grains.
Distilled Water	1 ounce.

The common table salt is often very impure, and therefore, if the pure Chloride cannot be obtained, Chloride of Ammonium (often termed *Muriate of Ammonia*) may be substituted.

Mix any number of ounces according to the above formula and add an equal bulk of the whites of new-laid eggs. Then with a bundle of quills tied together beat the whole into a perfect froth. As the froth forms it is to be skimmed off and placed in a flat dish to subside. The success of the operation depends entirely upon the manner in which this part of the process is conducted;—if the Albumen is not thoroughly beaten, flakes of animal membrane will be left in the liquid, and will certainly cause streaks upon the paper. Inexperienced operators frequently complain of these streaks, but if the eggs are fresh there is no difficulty whatever in obtaining a smooth and homogeneous liquid by proper frothing. When the froth has partially subsided, transfer it to a tall and narrow jar, and allow to stand for several hours, that the membranous shreds may settle to the bottom. Then pour off the upper clear portion, which is fit for use. Albuminous liquids are too glutinous to run well through a paper filter, and therefore it is better to clear them by subsidence.

The solution made according to these directions will contain exactly twenty grains of salt to the ounce, dissolved in equal parts of Albumen and water. Some operators employ the Albumen alone without any addition of water, but the paper in that case has a very highly varnished appearance, which is thought by most to be objectionable.

Mode of applying the Albumen to the paper.—Take a

sheet of the paper and examine it carefully by a strong light to find out the smooth side. There is a difference in this respect, the wire markings being more evident upon one side of the paper than upon the other.

Pour a portion of the Albumen solution into a flat dish to the depth of half an inch. Then, having previously cut the paper to the proper size, take a sheet by the two corners, bend it into a curved form, convexity downwards, and lay it upon the Albumen, the centre part first touching the liquid and the corners being lowered gradually. In this way all bubbles of air will be pushed forwards and excluded. One side only of the paper is wetted; the other remains dry. Allow the sheet to rest upon the solution for *three minutes*, and then raise it off, and pin up by two corners. If any circular spots, free from Albumen, are seen, caused by bubbles of air, replace the sheet for the same length of time as at first.

This albumenized and salted paper will keep any length of time in a dry place. Some have recommended to press it with a heated Italian iron, in order to coagulate the layer of Albumen upon the surface; but this precaution is unnecessary, since the coagulation is perfectly effected by the Nitrate of Silver used in the sensitizing. Also it is doubtful how far a very thin layer of Albumen would admit of coagulation by the simple application of a heated iron.

To render the paper sensitive.—This operation must be conducted by yellow light. Take of

Nitrate of Silver . . .	60 grains.
Distilled Water	1 ounce.

Prepare a sufficient quantity of this solution, and lay the sheet upon it in the same manner as before. If the Canson paper is used, at least five minutes must be allowed for the decomposition.

Some prefer to *brush* the Silver solution instead of applying it by floating, but in that case the proportions used must be different. Ten grains of salt to the ounce, in place of twenty, and 100 grains of Nitrate of Silver.

After the sensitizing solution of Nitrate of Silver has been in use some time, it becomes discoloured from a partial formation of Sulphuret of Silver. This may be obviated by the employment of Animal Charcoal,* but a better plan is to use the white china clay or "pipe-clay" for the same purpose. About twenty grains of this substance may be added to each ounce of the Silver solution, and kept constantly with it in the bottle, pouring off the upper clear portion for use.

After a large quantity of paper has been sensitized, it may be well to add fresh Nitrate of Silver, in the proportion of about ten grains to the ounce, in order to keep the Bath at its original strength.

Sensitive albumenized paper, prepared as above, will usually keep two or three days, if protected from the light, but eventually it turns yellow from partial decomposition.

C. PREPARATION OF AMMONIO-NITRATE PAPER.

Take of

Purified Gelatine	2 grains.
Chloride of Sodium or Ammonium .	20 grains.
Distilled Water	1 ounce.

Weigh out the proper quantity of Gelatine for the required number of ounces, and dissolve it in a small bulk of warm water. Then add the remainder of the water and the salt. The object is to employ so much Gelatine that the liquid will nearly, but not quite, gelatinize on

* Common Animal Charcoal contains Carbonate and Phosphate of Lime, which decompose the Nitrate of Silver; purified Animal Charcoal is usually acid from Hydrochloric Acid.

cooling. Its use appears to be to form a more even layer of salt upon the surface of the paper, but it is doubtful whether the tint of the finished Positive is much affected; certainly not to the same extent as when Albumen is used. The manner of salting the paper is in this case precisely the same as before; but if much Gelatine has been added, and the solution employed warm, it will be well to hang the sheets near to the fire, to prevent any gelatinizing, which might otherwise occur.

Mode of sensitizing the paper.—Gelatine paper may be sensitized with the ordinary 60-grain solution of Nitrate of Silver. The tint of the Positive in that case is very dark, but somewhat wanting in brilliancy. The use of Ammonio-Nitrate of Silver gives a certain depth and richness of colour which it is difficult to secure in the common way.

Preparation of Ammonio-Nitrate of Silver.—Take of

Nitrate of Silver	40 grains.
Distilled Water	1 ounce.

Dissolve the Nitrate of Silver in one-half of the total quantity of water. Then take a pure solution of Ammonia and drop it in carefully, stirring meanwhile with a glass rod. A brown precipitate of Oxide of Silver first forms, but on the addition of more Ammonia it is redissolved. When the liquid appears to be clearing up, add the Ammonia very cautiously, so as not to incur an excess. In order still further to secure the absence of free Ammonia, it is usual to direct, that when the liquid becomes perfectly clear, a drop or two of solution of Nitrate of Silver should be added until *a slight turbidity* is again produced. Lastly, dilute with water to the proper bulk. If the crystals of Nitrate of Silver employed contained a large excess of free Nitric Acid, it is possible that no precipitate will be formed on the first addition of Ammonia. The free Nitric Acid, producing *Nitrate of*

Ammonia with the alkali, keeps the Oxide of Silver in solution. This cause of error is not likely to happen frequently, since the amount of Nitrate of Ammonia required to prevent all precipitation would be considerable. Ammonio-Nitrate of Silver should be kept in a dark place, being more prone to reduction than the Nitrate of Silver.

Sensitizing the paper with the Ammonio-Nitrate.—This operation may be conducted precisely as before described under the head of Albumen paper (page 279). Many operators prefer brushing on the solution of Ammonio-Nitrate; but the above formula contains too much salt to be thoroughly decomposed by a 40-grain solution of Ammonio-Nitrate applied with a brush.

Therefore if the brush is used, reduce the salt to 12 grains, and increase the strength of the Ammonio-Nitrate to 80 grains to the ounce.

The operator however is recommended to commence by *floating* the paper, as an even layer of sensitive chloride, and a rich dark colour in the finished proof, is more easily obtained in that way.

Mode of sensitizing paper by brushing.—Brushes are sold, manufactured purposely for applying Silver solutions; but the hair is soon destroyed, unless care is taken to keep the brush clean. In sensitizing paper by brushing, lay the salted sheet upon blotting-paper, and wet it thoroughly by drawing the brush first lengthways and then across. Allow it to remain flat for a few minutes, in order that a sufficient quantity of the Silver solution may be absorbed, and then pin it up by the corner in the usual way.

Probably one reason why brushing is especially recommended with the Ammonio-Nitrate of Silver may be, that the properties of the solution are materially altered by the reaction with the salt; free Ammonia being formed, as is shown at page 189 of this Work. Hence a gradual

blackening and decomposition from presence of Chloride of Silver dissolved in the alkali.

Ammonio-Nitrate papers cannot be kept long: they become discoloured after the lapse of twelve to twenty-four hours.

SECTION II.

Preparation of the fixing and colouring solutions.

There are three different modes of preparing a Bath for fixing and colouring Positive proofs.—A. By means of Perchloride of Iron.—B. With Iodine.—C. With Chloride of Gold. These will be described successively, and afterwards proper directions given as to the management and peculiarities of each.

A. PREPARATION OF A FIXING AND COLOURING BATH WITH PERCHLORIDE OF IRON.

Take of

Solution of Perchloride of Iron	6 drachms.
Hyposulphite of Soda . . .	4 ounces.
Water	8 ounces.
Nitrate of Silver	30 grains.

The Hyposulphite of Soda is first dissolved in seven ounces of the water, the Nitrate of Silver in the remaining one ounce. The Perchloride of Iron is then poured into the solution of Hyposulphite by degrees, stirring all the time. The addition of the Iron salt strikes a fine purple colour, but this soon disappears. When the liquid has become again colourless, which it does in a few minutes, add the Nitrate of Silver, stirring briskly. Perfect solution will take place without any formation of Black Sulphuret.

In the reaction, the Perchloride of Iron is reduced to the condition of *Proto*chloride, and exists in the liquid in that form (see page 166). Consequently, if Carbonate

of Soda, or any alkali, be added to the Bath, a precipitate, either of Carbonate or Sulphuret of Iron, is formed (see page 178).

Perchloride of Iron in solution in Alcohol is sold by druggists under the name of 'Tincture of Muriate of Iron;' but it is better to prepare a Perchloride by diluting the yellow Muriatic Acid of commerce with an equal bulk of water, and boiling for a quarter of an hour with the red Oxide of Iron sold as 'Precipitated Carbonate of Iron.' About three drachms of the Oxide is sufficient for two ounces of the diluted Acid, and will leave an excess which afterwards sinks to the bottom. The clear solution of Perchloride being poured off, is fit for use; it contains usually a portion of free Hydrochloric Acid, but this produces no injurious effect.

B. PREPARATION OF A FIXING AND COLOURING BATH WITH IODINE.

Take of

Commercial Iodine . . .	30 grains.
Hyposulphite of Soda . .	4 ounces.
Water	8 ounces.
Nitrate of Silver	30 grains.

Dissolve the Nitrate of Silver in an ounce of the water, as before. Then, from the total quantity of Hyposulphite of Soda, weigh out carefully

Hyposulphite of Soda . .	60 grains.

Dissolve in an ounce of the water, and throw in the Iodine. Agitate the vessel until the whole has disappeared, which will happen in the course of a few minutes. If after the solution of the Iodine *a brown tint* is acquired, there is an excess of Iodine; in that case, cautiously add Hyposulphite of Soda, a single grain at a time, until the liquid becomes colourless, then pour in

Nitrate of Lead	40 grains

previously dissolved in an ounce of the water. The addition of Nitrate of Lead causes the separation of the greater portion of the Iodine in the form of yellow Iodide of Lead. Throw the whole upon a paper filter, and allow it to drain for a short time; then pour upon it by degrees two ounces of water, in order to wash out as much of the soluble Tetrathionate of Soda as possible. When all has run through, add the remaining three ounces of water; dissolve the Hyposulphite of Soda, and mix in the Nitrate of Silver solution with continual stirring as before.

C. PREPARATION OF A FIXING AND COLOURING BATH WITH CHLORIDE OF GOLD.

Take of

Solution of Chloride of Gold, a quantity equivalent to .	4 grains.
Nitrate of Silver	30 grains.
Hyposulphite of Soda . .	2 ounces.
Water	8 ounces.

Dissolve the Hyposulphite of Soda in four ounces of the water, the Chloride of Gold in three ounces, the Nitrate of Silver in the remaining ounce; then pour the diluted Chloride by degrees into the Hyposulphite, stirring meanwhile with a glass rod; and afterwards the Nitrate of Silver in the same way. This order of mixing the solutions is to be strictly observed: if it were reversed, the Hyposulphite of Soda being added to the Chloride of Gold, the result would be the reduction of metallic Gold. The difference depends upon the fact, that the Hyposulphite of Gold which is formed is an exceedingly unstable substance, and cannot exist in contact with unaltered Chloride of Gold. It is necessary that it should be dissolved by Hyposulphite of Soda *immediately* on its formation, and so rendered more permanent by conversion into a double salt of Soda and Gold.

D. GENERAL REMARKS UPON THE MANAGEMENT, ETC., OF THESE COLOURING BATHS.

Colouring Baths prepared with Tetrathionate of Soda, either by the Iodine or Perchloride of Iron process, are acid to test-paper at the expiration of a few hours after mixing. Also there is a considerable deposition of Sulphur, which may be removed by filtration, but this is scarcely necessary, the close texture of the paper upon which Positives are printed effectually preventing any solid matter in suspension from doing injury. In place of the Nitrate of Silver recommended in the formulæ, *Chloride of Silver* may be used, but not *Iodide of Silver*, as the formation of Iodide of Sodium would be objectionable (see page 182). For the same reason, it is better not to add any part of the Hypo Bath used for fixing Negatives to the Positive colouring solution.

The Perchloride of Iron Bath is decidedly more active than the second, with Iodine, if both are employed soon after their preparation. This is probably explained by the fact, that in the latter case the whole of the Iodine cannot be perfectly removed, Iodide of Lead being soluble to a minute extent in solution of Tetrathionate of Soda. The retarding effects produced by soluble Iodides in the Bath are shown at page 182. An excellent colouring Bath however can be prepared with Iodine, if a little longer time is allowed for the decomposition; indeed this is the case with all Tetrathionate colouring Baths—they work better at the expiration of a few days, or a week, from the time of mixing.

Directions for neutralizing.—The Tetrathionate Baths may be employed either in an acid or neutral state. If the weather is cold, probably the colouring action will be very slow, and in that case it is best to allow the acid to remain. But if the thermometer indicates 60° or higher,

the coloration of the print is effected with more rapidity, and there is danger of the half-tones being eaten away by the acid Bath (see page 175). The temperature of the solution is a most important point to be attended to in colouring by Tetrathionate: if it sinks to 40°, the addition of two or three drops of Acetic Acid will be useful (see page 183). In that case however the subsequent washing must be conducted with unusual care, since the smallest trace of free acid remaining in the fibres of the paper would eventually cause fading of the proof. Positives printed in a Bath to which Acetic or Hydrochloric Acid is added, are usually very black, but somewhat deficient in warmth and brilliancy; the half-tones are dissolved more than ordinarily, and there is a more marked tendency to yellowness of the whites.

In neutralizing a colouring Bath, if a strong alkali, or carbonate of an alkali, such for instance as Potash or Carbonate of Soda, be used, it is necessary to be careful not to add an excess, since if the solution were rendered thoroughly alkaline and set aside for a week, all colouring power would be destroyed. (See page 165.)

It is not certain that *Ammonia* produces an equally marked effect; and therefore the liquid may be *exactly neutralized* by a few drops of Ammonia. A more simple plan is to shake it up for five minutes with as much powdered chalk or whiting as will stand upon a shilling, and afterwards to allow it to subside, or to filter through blotting-paper. Indeed this plan with chalk is the only one practicable in the case of the Perchloride of Iron Bath, as the addition of an alkali would produce a precipitate of Sulphuret of Iron. (See page 178.)

After the Bath has been neutralized, there is a constant tendency to a return of the acidity. It has been shown, at page 170, that the continual décomposition which takes place in the solution produces free acid.

When the Bath is to be set aside, and its use discontinued for some time, add a few drops of any acid as a safeguard against alkalinity. (See page 172.)

The addition of fresh Tetrathionate to the Bath will scarcely be required, if a constant succession of prints are immersed as they are taken from the frame (see page 179); but much in this respect depends upon the temperature of the atmosphere, the generation of the colouring principle being certainly slower during cold weather.

If the operator desires at any time to prepare a colouring Bath with an unusual degree of energy, he may do so by adopting the Iodine process, and multiplying the quantity of Iodine and Nitrate of Lead four times, the other ingredients remaining the same. The Bath is to be set aside for three weeks, and then rendered perfectly neutral. In this way a very fine colour will be secured.

Remarks applying to the third formula with Chloride of Gold.—In the case of the third formula with Chloride of Gold, the action which takes place not being so thoroughly understood, it is more difficult to give explanation.

The *time of coloration* depends much upon the quantity of Gold present, and may in some cases be extended to many hours. The results of a few experiments, performed roughly, appeared to indicate that the activity of this Bath is less affected by depression of temperature than those prepared with Tetrathionate. Certainly the injurious effects of prolonged immersion are not so evident as with the first two formulæ;—the purity of the whites remains unaltered for many hours if the Bath is new, but with an old Bath there is a tendency to yellowness, which is probably caused by the presence of sulphuretted principles (p. 181). Fresh Chloride of Gold must be added from time to time as it appears to be required. A few drops of Acetic Acid (not more than two or three to half a pint) hasten the colouring action as described in the last page.

Hints in selecting from these formulæ.—The Gold Bath is the most simple and easy to work, since it requires no neutralizing or filtration, and the print can be left in for a long time with impunity. Formula No. 1, with Perchloride of Iron, is very active, but not adapted to the Ammonio-Nitrate paper. Formula No. 2 works slowly at first, and especially so in cold weather; but it possesses advantages in being free from any metallic salt, like the Protochloride of Iron, which is precipitated by alkalies; hence it can be used for any variety of sensitive paper, and may be neutralized by Ammonia in place of Carbonate of Lime. After a little experience, the operator will observe the peculiarities of tint yielded by each kind of Bath;—the Tetrathionate solutions give fine red purple and brown tints with albumen paper; pure blacks, but somewhat wanting in lustre, with gelatine paper sensitized with plain Nitrate; and rich velvety blacks with the Ammonio-Nitrate. The Gold Bath yields blue purples or blacks on the Albumen, and intense blacks with Gelatine or Ammonio-Nitrate.

SECTION III.

The Manipulatory Details of Photographic Printing.

The operator having prepared sensitive paper, and also the colouring Bath, according to directions recently given, proceeds, in the present Section, to the actual process of printing;—divided into—A. The exposure to light, or printing, properly so called.—B. The fixing and colouring, and—C. The washing, drying, and mounting of the proof.

A. THE EXPOSURE TO LIGHT.

For this purpose frames are sold, so constructed that they admit of being opened at the back, in order to ex-

amine the progress of the darkening by light, without producing any disturbance of position.

Simple squares of thick plate glass however succeed equally well, when a little experience has been acquired.

Supposing the frame to be employed, the shutter at the back is removed, and the Negative laid flat upon the glass, Collodion side uppermost. A sheet of sensitive paper is then placed upon the Negative, sensitive side downwards, and the whole tightly compressed by replacing and bolting down the shutter.

This operation may be conducted in the dark room; but unless the light is very strong, such a precaution will scarcely be required. The time of exposure to light varies much with the density of the Negative, and the power of the actinic rays as influenced by the season of the year and other obvious considerations. As a general rule, the best Negatives print slowly; whereas Negatives which have been under-exposed and under-developed are more rapid.

In the early spring or summer, when the light is powerful, probably about ten to fifteen minutes will be required; but as much as three-quarters of an hour may be allowed in the winter months, even in the direct rays of the sun.

It is always easy to judge of the length of time which will be sufficient, by exposing a small slip of the sensitive paper, *unshielded*, to the sun's rays, and observing how long it takes to reach the *coppery stage* of reduction. Whatever the time may be, about the same will be occupied in the printing, if the Negative is a good one.

When the darkening of the paper appears to have proceeded to a considerable extent, the frame is to be taken in and the picture examined. If simple squares of heavy plate glass are used in the place of a printing-frame, some difficulty will be experienced at first in returning the Negative precisely to its former position after the examina-

tion is complete, but this will easily be overcome by practice.

If the exposure to light has been sufficiently long, the general aspect of the print appears *decidedly darker* than it is intended to remain. The colouring Bath dissolves away the lighter shades and reduces the intensity, for which allowance is always made in the exposure to light. A little experience soon teaches what is the proper depth to print; but the following general rules may be useful as a guide;—Albumen pictures are more reduced by the colouring Bath than Ammonio-Nitrate pictures. The acid colouring Bath dissolves away the lighter shades more than the neutral Bath. When the proofs are to be immersed for a long time in order to secure black tones, it is necessary to over-print more strongly than when the purple tints are desired.

If, on removal from the printing-frame, a peculiar *spotted* appearance is seen, produced by unequal darkening of the Chloride of Silver, this shows that the Nitrate Bath was too weak, or the sheet removed from the surface too speedily.

On the other hand, if the general aspect of the print is a rich chocolate-brown in the case of Albumen, or a dark slate-blue with Gelatine or Ammonio-Nitrate paper, probably the subsequent coloration will proceed well. The tint however at this stage varies much with the strength of the Silver solution, and the mode of preparing the paper.

If, in the exposure to light, the dark shadows of the proof become decidedly *coppery* before the lights are sufficiently printed, the Negative is somewhat in fault. In that case, a better result will be obtained by reducing the amount of salt in the paper to one-half. Ammonio-Nitrate paper, highly salted, is particularly liable to this fault of excess of reduction, and especially so if the light

is powerful. Therefore the operator, when he has had experience, may with advantage modify the strength of the sensitizing solutions, taking as the minimum 40 grains of Nitrate of Silver and 10 grains of salt to the ounce.

B. THE FIXING AND COLOURING OF THE PROOF.

The print may be immersed in the colouring Bath immediately on its removal from the frame, but no injury results from putting it aside for a time, if it be kept in a dark place.

After its immersion, move it about for a short time to displace air-bubbles. In a few minutes the rich chocolate-brown or violet-blue tints disappear, and the red tones take their place.

Albumen proofs become brick-red; Gelatine and Ammonio-Nitrate a brownish black. The tint which will be ultimately acquired by the proof can be told with accuracy at an early period, if the operator is experienced and understands the working of the Bath;—if the colours are unusually pale and red, very probably the Silver Bath was too weak, or the time of contact insufficient;—a *pink* tint, in the case of Ammonio-Nitrate pictures, if very marked, generally gives a bad result. The action of the Bath must be continued until the desired effect is obtained. This may happen in from twenty minutes to half an hour, if the solution is in good working order and the thermometer at 60°; but everything depends upon temperature. In the case of the Chloride of Gold colouring Bath, no certain rule can be given; but the time of coloration will usually be longer than with Tetrathionate, even four to five hours not being too much in some cases. The purple tones are an earlier stage of coloration than the black tones, and therefore the latter require more time. It must be borne in mind, however, that prolonged immersion in a Tetrathionate Bath is decidedly favour-

able to yellowness of the whites, and with an Albumen print it will be difficult to obtain pure whites if the colouring is carried beyond the purple stage. With the Gold Bath the action may be pushed further with impunity.

Ammonio-Nitrate, and Gelatine papers are less prone to turn yellow than paper prepared with Albumen. The yellow colour is not often seen decidedly whilst the print is in the Bath, but it comes out in the after-processes of washing and drying.

The error most frequently committed in colouring Positive proofs is—continuing the action of the Hypo Bath for too long a time with the idea of obtaining darker tones. The injurious effects so caused are most evident when the print has been washed and dried; it is then seen that much of the brilliancy and richness of the tint is lost, whereas if the sheet had been removed at an earlier period, the action continuing slightly in the water, it would have been improved. These remarks apply in all cases, but especially so to the Tetrathionate Bath.

Some advise that on removal from the colouring Bath the print should be soaked in new Hypo for ten minutes, in order to complete the fixation, but this precaution is not required with solutions of such a strength as those given in the first two formulæ. An analysis of an old Hypo Bath which had been very extensively used, indicated only ten grains of Hyposulphite of Silver to the ounce, so that it was at that time far from being saturated.

In the third formula, with Chloride of Gold, the proportion of Hyposulphite being less, a new solution of the same strength may advantageously be employed after the other, and will serve to fill up the bottle and supply the loss caused by evaporation and use.

Also with a Bath prepared by the Perchloride of Iron process, if any red deposit upon the surface of the print

occurs during the washing, a portion of the Protochloride of Iron may be removed from the fibres of the paper by soaking in new Hypo.

The addition of fresh crystals of Hyposulphite of Soda occasionally, in order to keep up the strength of the Bath, is a safe plan to adopt, the exact quantity added not being material.

C. ON THE WASHING, DRYING, AND MOUNTING OF THE POSITIVE PROOFS.

If the view given in a former part of this Work of the chemical composition of the coloured surface which forms the Positive picture be correct (see page 178), it is evidently of the greatest importance as regards the permanence of the proof, to expend much pains in the after processes of washing and drying.

The first point to be attended to is, thoroughly to remove every trace of Hyposulphite of Soda from the fibres of the paper. Now Hyposulphite of Soda is a substance which adheres very closely to any body wetted by its solution, and therefore the print, on its removal from the colouring Bath, is to be placed in water and allowed to soak for several hours. The water must be changed two or three times, and at the last hot water may be substituted for cold. Complaints, however, are frequently made that the hot water injures the tint. If that is found to be the case, then use only cold water, but allow a proportionably longer time. The water employed for washing must be perfectly neutral. The addition of a single drop of any acid would have the effect of changing the purple tints to black from formation of Hyposulphurous Acid in the fibres of the paper.

When the washing is completed, the print may be suspended across a string or a glass rod, and allowed to dry. The fluid which drains from the lower edge can be tested

for Hyposulphite of Soda and Silver by the application of a drop of a dilute solution of the *Protonitrate of Mercury* —a black colour, which is *Sulphuret* of Mercury, indicates the presence of Hyposulphite. A more simple plan is to apply the tongue to the lower edge of the paper; if no sweet or metallic taste is perceptible, the print is sufficiently washed (see page 54).

When the print is nearly dry, it is recommended by some to place it between two layers of blotting-paper, and press with a moderately hot iron. This appears to darken the tint slightly if produced in a feeble colouring Bath, but when the Bath is active it causes but little appreciable change.

Lastly, in mounting the proofs, be careful not to employ sour paste, which may possibly injure the tint; and keep them in a place free from damp and mould.

CHAPTER VI.

ON THE MEANS OF PRESERVING THE SENSITIVENESS OF COLLODION PLATES.

THE great objection to the Collodion process has always been the difficulty of preserving the sensitiveness of the plates for any length of time. Hence it is necessary to prepare them immediately before they are required for use, which is not always convenient for tourists and operators working out-of-doors.

Many adopt the plan of carrying with them a small portable tent, covered in with folds of yellow calico, or they employ a Camera, so constructed that all the operations of sensitizing and developing the plate can be carried on within the body of the instrument.

Our present intention, however, is less to describe appliances of this kind than to show how the sensibility of the Collodion plates can be rendered more lasting, so that they may be employed many hours, or even days, after being excited.

If the film of Collodio-Iodide of Silver, after having been lifted out of the Bath, is allowed to dry spontaneously, the solution of free Nitrate of Silver upon the surface, becoming concentrated by evaporation, eats away the Iodide of Silver and destroys the film.

Mr. Archer proposed originally to obviate this by wash-

ing off the Nitrate with distilled water, but this plan injures the sensitiveness of the plate so much that it is difficult afterwards to obtain sufficient intensity for Negative pictures.

Other operators have attempted to prevent evaporation by the use of a second plate of glass in such a way as to *enclose* the sensitive film with an intervening stratum of liquid. The difficulty however of separating the glasses again, without tearing the film, is considerable.

No doubt the process lately devised by Messrs. Crookes and Spiller for preserving sensitized Collodion is more feasible than any which has preceded it. The plan proposed by these gentlemen is to make use of the well-known property possessed by certain saline substances of remaining in a moist condition for any length of time when once wetted. Such salts are termed "deliquescent," and many of them have so great an attraction for water that they absorb it eagerly from the air. The solution being once formed, the water cannot easily be driven off except by the application of a considerable heat.

In this process, then, the plate, after having been excited in the usual way, is coated on the surface with a solution of a deliquescent salt, by which the tendency to spontaneous evaporation is destroyed and the plate remains in a damp state for an indefinite period of time.

There are many deliquescent salts familiar to chemists, but a selection cannot be made from them indifferently. It is necessary that the salt should be neutral to test-paper, and also that it should produce no decomposition when added to solution of Nitrate of Silver. The Nitrates and Acetates both fulfil these conditions, but the latter only partially so. Acetate of Silver, being *but sparingly* soluble in water, is precipitated on mixing an Acetate with Nitrate of Silver, unless both solutions are dilute.

The *Nitrate of Zinc* was the salt originally selected by

Mr. Crookes, but difficulties arising in the manufacture on a large scale, the Nitrate of Magnesia has been substituted.

More recently still, Mr. Shadbolt, allowing the claims of Messrs. Crookes and Spiller to priority of publication, proposes to improve their process by substituting *Honey* for the Nitrate of Magnesia, as being more easily procurable and better in the result. Honey can scarcely be termed a deliquescent substance, but it possesses, like other uncrystallizable sugars, the property of remaining moist and sticky for a lengthened period of time. (For the chemistry of Honey, see Part III.)

The writer has not at present had the opportunity of fully testing the respective merits of these processes, and therefore he will take the liberty of transcribing from the original papers, published by the authors in the Journal of the Photographic Society, vol. ii.

THE NITRATE OF MAGNESIA PROCESS OF MESSRS. CROOKES AND SPILLER.

"The plate coated with Collodion in the usual manner, is to be rendered sensitive in a 30-grain Nitrate of Silver Bath, in which it should remain rather longer than is generally considered necessary (about five minutes); it must then be slightly drained, and immersed in a second Bath, consisting of

Nitrate of Magnesia . . .	4 ounces,
Nitrate of Silver	12 grains,
Glacial Acetic Acid . . .	1 drachm,
Water	12 ounces,

and there left for about five minutes, then removed and placed in a vertical position on blotting-paper, until all the surface-moisture has drained off and been absorbed; this

generally takes about half an hour, and they may then be packed away in any convenient box until required for use.

"Not only is the sensitiveness unimpaired by this treatment, but we think, on the contrary, that it is slightly increased; instantaneous Negatives have been taken on plates which had been prepared some days previously. We are not yet in a position to give the length of time that may elapse between the preparation of the plate and development of the picture: such experiments necessarily require a more lengthened period than we have at present been able to give, but as long as they have yet been kept (upwards of three weeks), there has been no appearance of deterioration.

"Before the development, we find it advisable to moisten the Collodion film by immersion in the Silver Bath for about half a minute, as otherwise the Pyrogallic Acid or Iron solution would not flow evenly over the plate. The fixing, etc., is of course conducted as usual.

"It will be as well to draw attention to a few points which, although not absolutely essential, may possibly be found useful in practice. The glass plates should be cleaned with more care than is necessary when they are to be used immediately; we have found strong Nitric Acid applied with a tooth-brush most convenient. With regard to the Collodion, we have tried very many different samples, and with tolerably uniform success. The greater number of our experiments have been made with a tolerably thick Collodion, the Alcohol and Ether of which were in the proportion of 1 : 2, made sensitive with four grains of Iodide and half a grain of Bromide of Ammonium to the fluid ounce. We have also employed a Collodion containing Iodide and Bromide of Cadmium with good success.

"Of the 30-grain Silver solution for exciting the plate

we have only to recommend the use of Acetic instead of Nitric Acid, to give the Bath that faintly acid reaction which is by some operators considered desirable.

"There are one or two circumstances to be attended to in the preparation of the Magnesia Bath. Commercial fused Nitrate of Magnesia is very liable to contain Chlorine, and also to have an alkaline reaction on account of the fusion being carried too far. Of course the quantities of Acetic Acid and Nitrate of Silver given in the formula for the Bath, are on the supposition that the Nitrate of Magnesia is pure; if this be not the case, it should be rendered perfectly neutral with Acetic Acid, the Chlorine exactly precipitated with Nitrate of Silver, and then the proper amounts of Acid and Silver added. However, if the impurities are very considerable, it will be safer to reject the salt at once. This Bath will keep in good order for a long time; the only point to be attended to is to drain the plates slightly after coming from the Silver Bath, and, if necessary, to remove the liquid from the back with blotting-paper, so as to introduce as little Silver as possible into the Nitrate of Magnesia. A solution of one grain of Silver to the ounce is quite sufficient to keep the plates sensitive; and when the strength rises, as it will in time, to above a certain limit, the slight evaporation that always takes place will render the Silver solution sufficiently strong to dissolve off the Iodide in small holes. If this occur, the Bath can be restored by nearly, but not quite, precipitating the Silver with a solution of Chloride of Magnesium, and then filtering.

"One of the most important things to be attended to, is the necessity of preserving the plates where they are perfectly free from any light. It will be evident to all, that anything short of absolute darkness, when the sensitive surface is exposed to its action for day after day, and perhaps week after week, must be fatal to its subsequent

cleanliness. The necessity for protecting the plates from any deleterious gases,—Ammonia, for instance,—is too obvious to require comment."

THE HONEY PROCESS OF MR. SHADBOLT.

"Having prepared and excited the Collodion in the usual manner, on its removal from the Bath of Nitrate of Silver it is to be drained pretty closely for about half a minute, and then immersed in a second Bath, consisting of distilled water 20 to 30 ounces to 1 ounce of the exciting Bath (the exact quantity is not of great moment), and allowed to remain in the latter mixture until the liquid flows evenly on lifting the plate up, which will happen in about from two to three minutes after immersion. The object of this proceeding is to wash away all but a slight trace of free Nitrate of Silver, as one of the causes of deterioration of the plate is the crystallization of this salt on the surface of the Collodion. This distilled water Bath should be in a vertical vessel, similar to that used for exciting, and the same Bath, if freed from impurities as they accumulate, will do for an indefinite time. To distinguish it, I shall term it the *washing Bath*.

"The plate may be removed from this Bath as soon as the liquid flows freely, and again drained closely, when a portion of the preservative syrup is to be poured on and off once or twice, being careful to avoid bubbles, or any minute particles of matter being left on the plate; which is then to be stood upright upon *clean* blotting-paper with the Collodion-side towards the wall to drain. In about ten minutes' time, the lower edge of the plate where the syrup has become collected, may be touched lightly with fresh blotting-paper to remove the superfluity, and then placed in the dark frame, or stored away in a box for future use. It is not *necessary* to perform *this* operation until convenient.

"The preservative syrup is thus made:—Take of *pure Honey* and *Distilled Water* equal parts by measure, mix thoroughly and filter. In my former directions a sixth part of the volume of Alcohol was included; but further experience leads me to consider this unnecessary, if not detrimental.

"If thoroughly excluded from the action of light, plates thus prepared will keep good for a *very long time*. The sensibility is certainly less than when fresh plates are used, and I judge that the exposure required is about double the time, for the same Collodion, if used immediately after its removal from the Nitrate Bath; but I cannot detect any further diminution for the first twenty-four hours, and I have taken a picture no less than three weeks after excitation, but with at least four times the exposure required for a fresh plate. I do not however recommend the plates to be kept longer than is really necessary, as the chances of change from very little actinic force are certainly great.

"The plates may be developed even as long as twelve hours after exposure. This part of the process is conducted as follows:—

"The plate is to be again immersed in the washing Bath and left from one to ten minutes to soak, occasionally lifting it up and down to facilitate the removal of the superfluous syrup, and thoroughly to soften what remains upon the plate. The longer the latter has been kept, the longer it should be allowed to soak.

"When taken out, a sufficient quantity of the developing solution is to be poured over the plate in the ordinary way, and, *provided the plate has been properly soaked* in the washing Bath, there is no greater difficulty experienced in getting it to flow over, than when a fresh plate is used. The image should appear very slowly, and when all the details are out *but very faint;* the developing solution is

to be returned into the measure (*taking especial care not to allow the small portion remaining on the plate to run in lines*), a feat readily performed if done quickly, and the plate instantly restored to a horizontal position. A small quantity of the *exciting Bath* (a 30-grain solution of Nitrate of Silver), from an eighth to a sixth of the volume of the solution that was poured from the plate into the measure, together with a like proportion of the preservative syrup, should now be added to the liquid in the measure and well mixed up; this is to be poured on the plate and kept moving until the picture is sufficiently intense, which can be carried to any degree if the exposure has been proportionately prolonged. So intense *can* the high lights be made, that a whole day's exposure to *direct sunshine* will not print through them. Of course I only mention this to show what can be effected—not what is desirable.

"The developing solution I usually adopt consists of 1 grain to the ounce of water solution of Pyrogallic Acid, one-fourth of the menstruum being the ordinary Acetic Acid of the druggists, or, if *glacial* Acetic Acid is used, one-twelfth part is sufficient.

"When sufficiently developed, the picture is washed and fixed as usual, either with Hyposulphite of Soda or Cyanide of Potassium, as may be preferred."

PART III.

OUTLINES OF GENERAL CHEMISTRY.

OUTLINES OF GENERAL CHEMISTRY.

CHAPTER I.

THE CHEMICAL ELEMENTS AND THEIR COMBINATIONS.

THE limits of the present Work will not allow of more than a simple sketch of the subjects which it is proposed to treat in this Chapter. Our attention therefore must be confined to an explanation of certain points which are alluded to in the first part of the work, and without a proper understanding of which it will be impossible for the reader to make any progress.

The following division may be adopted:—A. The more important elementary bodies, with their symbols and atomic weights.—B. The compounds formed by their union.—C. The class of salts.—D. Illustrations of the nature of chemical affinity.—E. Chemical nomenclature.—F. Symbolic notation.—G. The laws of combination.—H. The Atomic theory.—I. The chemistry of organic bodies.

A. THE CHEMICAL ELEMENTS, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

The class of elementary bodies embraces all those substances which cannot, in the present state of our knowledge, be resolved into simpler forms of matter.

The Chemical Elements are divided into "metallic" and "non-metallic," according to the possession of certain general characters.

The following are some of the principal non-metallic elements, with the symbols employed to designate them, and their atomic weights:*—

		Symbol.	Atomic Wt.
Gases.	Oxygen	O	8
	Hydrogen	H	1
	Nitrogen	N	14
	Chlorine	Cl	36
Solids.	Iodine	I	126
	Carbon	C	6
	Sulphur	S	16
	Phosphorus	P	32
Liquid.	Bromine	Br	78
Unknown.	Fluorine	F	19

The metallic elements are more numerous. The following list includes only those which are commonly known:—

		Symbol.	Atomic Wt.
Metals of the Alkalies.	Potassium	K	40
	Sodium	Na	24
Metals of the Alkaline Earths.	Barium	Ba	69
	Calcium	Ca	20
	Magnesium	Mg	12
Metals Proper.	Iron	Fe	28
	Zinc	Zn	32
	Cadmium	Cd	56
	Copper	Cu	32
	Lead	Pb	104
	Tin	Sn	59
	Arsenic	As	75
	Antimony	Sb	129

* For an explanation of these terms, see the latter part of the Chapter.

		Symbol.	Atomic Wt.
Noble Metals.	Mercury	Hg	202
	Silver	Ag	108
	Gold	Au	200
	Platinum		99

B. ON THE BINARY COMPOUNDS OF THE ELEMENTS.

Many of the elementary bodies exhibit a strong tendency to combine with each other, and so to form *compounds* which differ in properties from either of their constituent elements. This attraction, which is termed "chemical affinity," is exerted principally between bodies which are opposed to each other in their general characters. Thus, taking for example the elements Chlorine and Iodine—they are analogous in their reactions, and therefore there is but little attraction between them, whereas either of the two combines eagerly with Hydrogen, which is an element of a different class. So again, Sulphur unites with the metals, but two metallic elements are comparatively indifferent to each other.

Oxygen is by far the most important in the list of chemical elements. It combines with all the others, with the single exception perhaps of Fluorine. The attraction, or chemical affinity, however, which is exerted, varies much in different cases. The metals, as a class, are easily oxidized; whilst many of the non-metallic elements, such as Chlorine, Iodine, Bromine, etc. exhibit but little affinity for Oxygen. Also *Nitrogen* is a peculiarly negative element, showing little or no tendency to unite with either of the others.

Classification of binary compounds containing Oxygen.—When one simple element unites with another, the product is termed a "binary" compound.

There are two distinct classes of binary compounds of Oxygen;—first, *neutral* and *basic* Oxides, as *e. g.* the

Oxide of Hydrogen, or Water; the Oxide of Potassium, or Potash; the Oxide of Silver.

Water is termed a *neutral* oxide, because its affinities are low, and it is comparatively indifferent to other bodies. Potash and Oxide of Silver are *basic* oxides, and possess more chemical energy; but there is a great difference between the two in this respect, the former belonging to a superior class of bases, viz. the alkalies.

General characters of the Alkalies.—By studying the properties of an alkali (such as Potash or Soda) which are familiar to all, we gain a correct notion of the whole class of basic oxides. An alkali is a substance readily soluble in water, and yielding a solution which has a slimy feel from its solvent action upon the skin. It immediately restores the blue colour of reddened litmus, and changes the blue infusion of cabbage to green. Lastly, it is neutralized and loses all its characteristic properties upon the addition of any acid.

The *weaker bases* are, as a rule, sparingly or not at all soluble in water, neither have they the same caustic and solvent action upon the skin; but they restore the colour of reddened litmus, and neutralize acids in the same manner as the more powerful bases or alkalies.

Second class of the binary compounds of Oxygen, or Acid *Oxides.*—This class, taking the stronger acids as the type of all, may be described as follows:—very soluble in water, the solution possessing an intensely sour taste, and a *corroding* rather than a solvent action upon the skin; it changes the blue colour of litmus, and other vegetable substances, to red, and neutralizes the alkalies and basic oxides generally.

Observe however that these properties are possessed in very various degrees by different acids. Prussic Acid and Carbonic Acid, for instance, are not sour to the taste, and, being feeble in their reactions, redden litmus scarcely or

not at all. All acids however, without any exception, tend to combine with bases, and to neutralize themselves in that way, so that this may be said to be the most characteristic property of the class.

Chemical composition of acid and basic Oxides contrasted.—It is a law commonly observed, although with many exceptions, that bases are formed by the union of Oxygen with *metals*;—and acids, by Oxygen uniting with *non-metallic elements*. Thus, Oil of Vitriol is a compound of Sulphur and Oxygen; Aqua-fortis, of Nitrogen and Oxygen; but Potash is an Oxide of Potassium, which is a metal, and the Oxides of Iron, Silver, Zinc, etc. are all bases, and not acids.

Again, the composition of acids and bases is different in another respect; the former invariably contain more Oxygen in proportion to the other element than the latter. Taking the same examples as before, the two classes may be represented thus:—

Acids	Oil of Vitriol,	Sulphur 1 atom,	Oxygen 3 atoms.
	Aqua-fortis,	Nitrogen 1 ,,	Oxygen 5 ,,
Bases	Oxide of Silver,	Silver 1 atom,	Oxygen 1 atom.
	Oxide of Iron,	Iron 1 ,,	Oxygen 1 ,,

On the class of Hydrogen Acids.—Oxygen is so essentially the element which forms the acidifying principle of acids, that its very name is derived from that fact (*οξυς, acid,* and *γενναω, to generate*). Still there are exceptions to this rule, and in some acids *Hydrogen* appears to play the same part; the *Hydracids*, as they are termed, are formed principally by Hydrogen uniting with elements like Chlorine, Bromine, Iodine, Fluorine, etc. Thus, Muriatic or Hydrochloric Acid contains Chlorine and Hydrogen; Hydriodic Acid contains Iodine and Hydrogen.

Observe, however, that the position held by the Hydrogen in these compounds is different from that of the Oxy-

gen in the "Oxyacids" as regards the number of atoms usually present; thus

Aqua-fortis = Nitrogen 1 atom, Oxygen 5 atoms
Muriatic Acid = Chlorine 1 „ Hydrogen 1 „

so that the composition of the Hydracids is analogous to the *basic* oxides in containing a single atom of each constituent.

C. ON THE TERNARY COMPOUNDS OF THE ELEMENTS.

As the various elementary substances unite with each other to form binary compounds, so these binary compounds again unite and form *ternary* compounds.

Compound bodies however do not, as a rule, unite with simple elements. In illustration, take the action of Nitric Acid upon Silver, described at page 15. No effect is produced upon the metal until *Oxygen* is imparted; then the Oxide of Silver so formed dissolves in the Nitric Acid—in other words, it is necessary that a binary compound should be first formed before the solution can take place.

The mutual attraction or chemical affinity exhibited by compound bodies is, as in the case of elements, most strongly marked when the two substances are opposed to each other in their general properties.

Thus, *acids* do not unite with other acids, but they combine instantly with *alkalies*, the two mutually neutralizing each other and forming "a salt."

Salts therefore are ternary compounds, produced by the union of acids and bases; common Salt, formed by neutralizing Muriatic Acid with Soda, being taken as the type of the whole class.

General characters of the Salts.—An aqueous solution of Chloride of Sodium, or common Salt, possesses those characters which are usually termed saline: it is neither sour nor corrosive, but, on the other hand, has a cooling, agree-

able taste. It produces no effect upon litmus and other vegetable colours, and is wanting in those energetic reactions which are characteristic of both acids and alkalies: hence, although formed by the union of two binary compounds, it differs essentially in properties from both.

All salts however do not correspond to this description of the properties of Chloride of Sodium. The Carbonate of Potash, for instance, is an acrid and alkaline salt, and the Nitrate of Iron reddens litmus-paper. A little reflection shows the cause of such differences. A perfectly neutral salt is formed when a strong acid unites with an equally energetic base; but if, of the two constituents, one is more powerful than the other, then the reactions of that one are seen to a certain extent in the resulting salt. Thus the Nitrate of Iron reddens the vegetable colour, because the Oxide of Iron, or *base* of the salt, is inferior in chemical energy to the Nitric Acid; and the Carbonate of Potash is *alkaline* to test-paper from a cause exactly the reverse; but if Nitric Acid and Soda are brought together, then a *Nitrate of Soda* is produced which is *neutral* in every sense of the term.

The Chloride of Sodium and salts of a similar kind are freely soluble in water, but all salts are not so. Some dissolve only sparingly, and others not at all. The Chloride and Iodide of Silver are examples of the latter class; they are not bitter and caustic like the Nitrate of Silver, but are perfectly tasteless, from being insoluble in the fluids of the mouth.

Therefore it is seen from these examples, and many others which might be adduced, that the popular notion of a saline body is far from being correct, and that, in the language of strict definition, any substance is a salt which is produced by the union of an acid with a base, altogether independent of the properties it may possess.

Thus *Cyanide of Potassium* is a true salt, although

highly poisonous; *Lunar Caustic*, or Nitrate of Silver, is a salt; the blue Sulphate of Copper is a salt; so also is Chalk or Carbonate of Lime, which has neither taste, colour, nor smell.

On the "Hydracid" class of Salts.—The distinction between Oxyacids and Hydracids has already been pointed out, and the latter shown to consist of Hydrogen united with elements analogous in their reactions to Chlorine, Iodine, Bromine, etc.

In a salt formed by an Oxygen Acid, both the basic and acid constituents appear. Thus the common *Nitre*, which is a Nitrate of Potash, is found by analysis to contain Oxide of Potassium as a base, and Aqua-fortis, so called, as an acid. But if a salt is formed by neutralizing an alkali with *a Hydrogen Acid*, the product in that case does not contain all the elements. This is seen from the following example:—

Hydrochloric Acid + Soda
= Chloride of Sodium + Water;

or, stated more at length,—

(Chlorine Hydrogen) + (Oxygen Sodium)
= (Chlorine Sodium) + (Oxygen Hydrogen).

Observe that the Hydrogen and Oxygen, being present in the correct proportions, unite to form Water, which is an Oxide of Hydrogen. This water passes off when the solution is evaporated, and leaves the dry crystals of salt. On the other hand, with the Oxyacid Salts, the elementary Hydrogen being absent, no water is formed, and the Oxygen remains.

Therefore it must be borne in mind that salts like the Chlorides, Bromides, Iodides, etc., contain only *two* elements, but that in the Oxyacid Salts, such as Sulphates, Nitrates, Acetates, *three* are present. Thus Nitrate of Silver consists of Nitrogen, Oxygen, and Silver, but Chlo-

ride of Silver has simply Chlorine and metallic Silver united, without Oxygen.

The separated Hydrogen and Oxygen again absorbed in the decomposition of Hydracid Salts.—If a portion of a Hydracid Salt,—such, for instance, as the Iodide of Potassium,—be dissolved in water, and a small quantity of Oil of Vitriol, or Sulphuric Acid, added, this Oil of Vitriol being very powerful in its chemical affinities, tends to destroy the existing salt and to appropriate to itself the base;—but observe—it does not remove *Potassium* and liberate *Iodine*, but it takes the *Oxide* of Potassium and sets free *Hydriodic Acid*. In other words, as an atom of water is produced during the *formation* of a Hydracid Salt, so is an atom destroyed and made to yield up its elements in the *decomposition* of a Hydracid Salt.

The reaction of dilute Sulphuric Acid upon Iodide of Potassium may be stated thus:—

Sulphuric Acid *plus* (Iodine Potassium) *plus* (Hydrogen Oxygen) *equals* (Sulphuric Acid, Oxygen Potassium) or Sulphate of Potash,
and (Hydrogen Iodine) or Hydriodic Acid.

D. THE NATURE OF CHEMICAL AFFINITY FURTHER ILLUSTRATED.

Illustration from the non-metallic elements.—If a stream of Chlorine gas be passed into a solution containing the same salt as before mentioned, viz. the Iodide of Potassium, the result is to liberate a certain portion of Iodine, which dissolves in the liquid, and tinges it of a brown colour. The element Chlorine, possessing a degree of chemical energy superior to that of Iodine, prevails over it, and removes the Potassium with which the Iodine was previously combined.

Chlorine + Iodide of Potassium
= Iodine + Chloride of Potassium.

The same law illustrated by the Metals.—A strip of Iron dipped in solution of Nitrate of Silver becomes immediately coated with metallic Silver; but a piece of Silver-foil may be left for any length of time in Sulphate of Iron without undergoing change: the difference depends upon the fact, that metallic Iron has a greater attraction for Oxygen than Silver, and hence it displaces it from its solution.

Iron + Nitrate of Silver
= Silver + Nitrate of Iron.

Illustrations amongst Binary Compounds.—If a few drops of solution of Potash or Ammonia (for the Chemistry of Ammonia, see page 334) be added to solution of Nitrate of Silver, a brown deposit is formed, which is the Oxide of Silver, insoluble in water: hence it is seen that as a stronger metal displaces *metallic Silver*, so does an *oxide* of the same metal displace *Oxide of Silver*. Therefore, bases like the alkalies, alkaline earths, etc. cannot exist in a free state in solutions of the salts of weaker bases (see page 106).

In the list given at page 308, the metallic elements are arranged principally in the order of their chemical affinities, those of Potassium, Sodium, Barium, etc. being by far the most marked.

The same law also applies to binary compounds possessing acid properties,—that is, the strong acids invariably displace those which are weaker from their salts, and appropriate the base. Thus, taking two illustrations familiar to Photographers:—

Sulphuric Acid + Nitrate of Potash
= Nitric Acid + Sulphate of Potash.

And again,

Nitric Acid + Acetate of Silver
= Acetic Acid + Nitrate of Silver.

It is not easy to arrange the acids in a list exactly according to their affinities, but usually the Oil of Vitriol, or Sulphuric Acid, is placed first, and the Carbonic Acid, which is a gaseous substance, last. The vegetable acids, such as Acetic, Tartaric, etc. are *intermediate*, being weaker than the mineral acids, but stronger than the Carbonic, and Prussic or Hydrocyanic, Acids.

The order of decompositions affected by the insolubility, or the volatility, of the products which may be formed.—It might be inferred, perhaps, from remarks already made, that on mixing saline solutions, a gradual interchange of elements would invariably take place, until the strongest acids were associated with the strongest bases, and *vice versâ*. There are many causes however which interfere to prevent this. One of these causes is *volatility*. As an illustration, take two acids, the *Sulphuric* and the *Phosphoric*;—of these, the former is ordinarily reputed the most powerful, and such it undoubtedly is at low temperatures; but Sulphuric Acid is volatile when strongly heated, whereas Phosphoric is perfectly fixed, even in the fire. Hence, if Phosphoric Acid be added to a salt of Sulphuric Acid, as *e. g.* the Sulphate of Soda, and a strong heat applied, the Sulphuric Acid is displaced and escapes in the gaseous form.

Ammonia is a powerful alkaline substance; but on account of its volatility it is driven off from its salts by the addition of a comparatively feeble base;—in fact, the same substance which Ammonia displaces at common temperatures, displaces Ammonia at *high* temperatures.

Observe also the violent effervescence which takes place on treating a *Carbonate* of any kind with an acid. The gaseous nature of Carbonic Acid, and its escape in that form, much facilitates the decomposition.

Insolubility is also a cause which exercises a great influence on the result which will follow in mixing solutions.

If the formation of an insoluble substance is possible by any interchange of elements, it will certainly take place. A solution of Chloride of Sodium added to Nitrate of Silver invariably produces Chloride of Silver; but nothing can be inferred from this fact, as to the relative chemical affinities of the two acids, since it is the *insolubility* of Chloride of Silver which determines its formation.

So again the *Nitrate of Iron* is produced by mixing Nitrate of Lead with Sulphate of Iron; but if an attempt is made to substitute Nitrate of *Potash* for the Nitrate of Lead, the result is uncertain, because, in such a case, there are no elements present which can, by interchanging, form an insoluble salt. Sulphate of Potash, although *sparingly* soluble in water, is not absolutely insoluble, like the Sulphate of Lead or the Sulphate of Baryta.

E. ON CHEMICAL NOMENCLATURE.

The nomenclature of the chemical *elements* is mostly independent of any rule; but an attempt has been made to obviate this in the case of those of later discovery. Thus the names of the newly-found *metals* usually end in "um," as Potassium, Sodium, Barium, Calcium, etc.; also those elements which possess analogous characters have corresponding terminations assigned to them, as Chlorine, Bromine, Iodine, Fluorine, etc.

Nomenclature of Binary Compounds.—These are often named by attaching the termination "ide" to the more important element of the two; as, the Ox*ide* of Hydrogen, or Water; the Chlor*ide* of Silver; the Sulph*ide* of Silver. Binary compounds of Sulphur, however, are often termed Sulphurets, as the *Sulphuret* or the *Sulphide* of Silver indifferently.

When the same body combines with Oxygen, or the corresponding element, in more than one proportion, the prefix "proto" is applied to that containing the least

Oxygen; "sesqui" to that with one and a half as much as the "proto;" "bi" or "bin" to that with twice as much; and "per" to the one containing the most Oxygen of all. As examples, take the following:—the Protoxide of Iron; the Sesquioxide of Iron; the Protochloride of Mercury; the Bichloride of Mercury. In these examples the *Sesquioxide* of Iron is also a *Per*oxide, because no higher simple oxide is known, and the *Bichloride* of Mercury is a *Per*chloride for a similar reason.

When an inferior compound is discovered, it is often termed "sub;" as the Suboxide of Silver; the Subchloride of Silver. These bodies contain the least known quantity of Oxygen and Chlorine respectively, and are hence entitled to the prefix "proto;" but being of minor importance, they are excepted from the general rule.

The combinations of metallic elements with each other are termed "alloys;" or if containing Mercury, "amalgams."

Nomenclature of Binary Compounds possessing acid properties.—These are named on a different principle. The termination "ic" is applied to one element. Thus, taking as an illustration the liquid known as "Oil of Vitriol," it is truly an *Oxide* of Sulphur, but as it possesses strong acid properties it is termed Sulphur*ic Acid*. So Nitric Acid is an Oxide of Nitrogen; Carbonic Acid is an Oxide of Carbon, etc. When there are two oxides of the same element, both possessing acid properties, the most important has the termination "ic," and the other "ous;" as Sulphuric Acid, Sulphur*ous* Acid; Nitric Acid, Nitr*ous* Acid.

Nomenclature of the Hydracids.—The Hydrogen Acids are distinguished from Oxyacids by retaining the names of both constituents, the termination "ic" being annexed as usual. Thus, *Hydro*chloric Acid, or the Chloride of Hydrogen; *Hydr*iodic Acid, or the Iodide of Hydrogen.

Further illustrations of the nomenclature of Binary

Compounds.—The Oxides of Nitrogen, and also of Sulphur, afford an interesting illustration of the principles of nomenclature. The former are as follows :—

	Nitrogen.	Oxygen.
Protoxide of Nitrogen . . .	1 atom.	1 atom.
Binoxide of Nitrogen . . .	1 „	2 „
Nitrous Acid	1 „	3 „
Peroxide of Nitrogen . . .	1 „	4 „
Nitric Acid	1 „	5 „

Observe, that two only out of the five possess acid properties, the others being simple oxides. Nitric Acid is, strictly speaking, the "Peroxide," but as it belongs to the class of acids, that term naturally falls to the compound below.

The binary compounds of Sulphur with Oxygen all possess acid properties; they may be represented (in part) as follows :—

	Sulphur.	Oxygen.
Hyposulphurous Acid . .	2 atoms.	2 atoms.
Sulphurous Acid	1 „	2 „
Hyposulphuric Acid . . .	2 „	5 „
Sulphuric Acid	1 „	3 „

In this case the Sulphuric and Sulphurous Acids had become familiarly known before the others, intermediate in composition, were discovered. Hence, to avoid the confusion which would result from changing the nomenclature, the new bodies are termed *Hypo*sulphuric and *Hypo*sulphurous (from *ὑπο*, *under*).

Nomenclature of Salts.—Salts are named according to the acid they contain, the termination "ic" being changed into "ate," and "ous" into "ite;" thus, Sulphuric Acid forms Sulph*ates*; Nitric Acid, Nitr*ates*; but Sulphur*ous* Acid forms Sulph*ites*, and Nitrous Acid, Nitr*ites*.

In naming a salt, the *base* is always placed after the acid, the term *oxide* being omitted; thus, *Nitrate of Oxide*

of Silver is more shortly known as "Nitrate of Silver," the presence of Oxygen being understood.

When there are two oxides of the same base, both of which are *salifiable*,—in naming the salts, the term "proto" is prefixed to the acid of the salt formed by the lowest, and "per" to that of the higher oxide; as, the *Proto*-sulphate of Iron, or Sulphate of the Protoxide; the *Per*-sulphate of Iron, or Sulphate of the Peroxide.

Many salts contain more than one atom of acid to each atom of base. In that case, the usual prefixes expressive of quantity are adopted; thus, the *Bi*sulphate of Potash contains twice as much Sulphuric Acid as the neutral Sulphate; the *Sesqui*carbonate of Soda $1\frac{1}{2}$ times as much Carbonic Acid as the ordinary Carbonate.

On the other hand, there are salts in which the base is in excess with regard to the acid, and which are usually known as "basic salts;" thus the red powder which deposits from solution of Sulphate of Iron is a *basic* Persulphate of Iron, or a Sulphate of the Peroxide of Iron with more than the normal proportion of oxide.

Nomenclature of the Hydracid Salts.—The composition of these salts being different from those formed by Oxygen Acids, the nomenclature varies also. Thus, in neutralizing Hydrochloric Acid with Soda, the product formed is not known as Hydrochlorate of Soda, but as *Chloride of Sodium;* this salt, and others of a similar constitution, being *binary*, and not *ternary*, compounds. The salt produced by Hydrochloric Acid and *Ammonia*, however, is often called "Muriate, or Hydrochlorate of Ammonia," although more strictly it should be the *Chloride of Ammonium*.

F. ON SYMBOLIC NOTATION.

The list of symbols employed to represent the various elementary bodies is given at page 308.—Commonly the initial letter of the Latin name is used, a second, or

smaller, letter being added when two elements correspond in their initials: thus C stands for Carbon, Cl for Chlorine, Cd for Cadmium, and Cu for Copper.

The chemical symbol however does not simply represent a particular element; it denotes also a definite weight, or equivalent proportion of that element. This will be explained more fully in the next page, whilst speaking of the Laws of Combination.

Formulæ of Compounds.—In the *nomenclature* of compounds it is usual to place the Oxygen or analogous element *first* in the case of binary compounds, and the acid before the base with the ternary compounds, or salts; but in representing them symbolically this order is reversed: thus, Oxide of Silver is written AgO, and never as OAg; Nitrate of Silver as AgO NO_5, not NO_5 AgO.

The juxtaposition of symbols expresses combination; thus, FeO is a compound of one proportion of Iron with one of Oxygen, or the "Protoxide of Iron;" if more than one equivalent is present, small figures are placed below the symbols; thus, Fe_2O_3 represents two equivalents of Iron united with three of Oxygen, or the "Peroxide of Iron;" SO_3, one equivalent of Sulphur with three of Oxygen, or Sulphuric Acid.

Larger figures placed before and in the same line with the symbols, affect the *whole compound* which the symbols express; thus, 2 SO_3 means two equivalents of Sulphuric Acid; 3 NO_5, three equivalents of Nitric Acid. The interposition of a *comma* prevents the influence of the large figure from extending further. Thus the double Hyposulphite of Soda and Silver is represented as follows:—

$$2\,NaO\,S_2O_2,\,AgO\,S_2O_2,$$

or *two* equivalents of Hyposulphite of Soda with *one* of Hyposulphite of Silver; the large figure referring only to the first half of the formula. Sometimes however

brackets, etc. are employed, in order to render a complicated formula more plain. For example, the formula for the double Hyposulphite of Gold and Soda, or the "Sel d'Or," may be written thus :—

$$3\,(NaO\,S_2O_2)\,AuO\,S_2O_2 + 4\,HO.$$

In this formula the *plus* sign (+) denotes that the four atoms of water which follow are less intimately united with the framework of the salt than the other constituents. The use of a *plus* sign is commonly adopted in representing salts which contain water of crystallization. Thus the formula for the crystallized Protosulphate of Iron is written as follows :—

$$FeO\,SO_3 + 7\,HO.$$

These atoms of water are all driven off by the application of heat, leaving a white substance, which is the anhydrous salt, and would be written simply as $FeO\,SO_3$.

The *plus* sign however is often employed in token of simple *addition*, no combination of any kind being intended. Thus the decomposition which follows on mixing Chloride of Sodium with Nitrate of Silver may be written as follows :—

$$NaCl + AgO\,NO_5 = AgCl + NaO\,NO_5;$$

that is—

Chloride of Sodium *added to* Nitrate of Silver
= Chloride of Silver *and* Nitrate of Soda.

G. ON EQUIVALENT PROPORTIONS.

When elementary or compound bodies enter into chemical union with each other, they do not combine in indefinite proportions, as in the case of a mixture of two liquids, or the solution of a saline body in water. On the other hand, a certain definite weight of the one unites with an equally definite weight of the other, and if an excess of either is present, it remains free and uncombined.

Thus, if we take *a single grain* of the element Hydrogen —to convert that grain into Water there will be required exactly 8 grains of Oxygen; and if a larger quantity than this were added, as for instance 10 *grains*, then two grains would be over and above. So, to form *Hydrochloric Acid*, 1 grain of Hydrogen takes 36 grains of Chlorine;—for the *Hydriodic Acid*, 1 grain of Hydrogen unites with 126 grains of Iodine.

Again, if separate portions of metallic Silver, of 108 grains each, are weighed out,—in order to convert them into Oxide, Chloride, and Iodide of Silver respectively, there would be required

Oxygen	8 grains.
Chlorine	36 „
Iodine	126 „

Therefore it appears that 8 grains of Oxygen are *equivalent* to 36 grains of Chlorine, and to 126 grains of Iodine, seeing that these quantities all play the same part in the reaction; and so it is with regard to the other elements—to every one of them a figure can be assigned which represents the number of parts by weight in which that element combines with others. These figures are the "equivalents" or "combining proportions," and they are denoted by the *symbol* of the element. A symbol does not stand as a simple representative of an element, but as a representative of *one equivalent* of an element. Thus "O" indicates 8 parts by weight of Oxygen; Cl one equivalent, or 36 parts by weight, of Chlorine; and so with the rest.

Observe however that these figures thus termed "equivalents" do not refer to the *actual number* of parts by weight, but only the *ratio* which exists between them: if Oxygen is 8, then Chlorine is 36, but if we term Oxygen 12, then Chlorine would be 54.

In the scale of equivalents now usually adopted, Hydro-

gen, as being the lowest of all, is taken as unity, and the others are related to this.

Equivalents of Compounds.—The law of equivalent proportions applies to compounds as well as to simple bodies, the combining proportion of a compound being always the *sum* of the equivalents of its constituents. Thus Sulphur is 16, and Oxygen 8, therefore Sulphuric Acid, or SO_3, equals 40. The equivalent of Nitrogen is 14, that of Nitric Acid, or NO_5, is 54. So also with regard to salts. Take, for instance, the Nitrate of Silver: it contains

	Equivalent.
Nitrogen	14
6 Oxygen	48
Silver	108
Total of equivalents, or equivalent of the Nitrate of Silver . . .	170

Practical application of the Laws of Combination.—The utility of being acquainted with the law of combining proportions is obvious when their nature is understood. As bodies both unite with and replace each other in equivalents, a simple calculation shows at once how much of each element or compound will be required in a given reaction. Thus, supposing it is desired to convert 100 grains of Nitrate of Silver into *Chloride* of Silver, the weight of salt which will be necessary is deduced thus:—one equivalent, or 170 parts, of Nitrate of Silver, is decomposed by an equivalent, or 60 parts, of Chloride of Sodium. Therefore

as 170 : 60 :: 100 : 35·2;

that is, 35·2 grains of salt will precipitate, in the state of Chloride, the whole of the Silver contained in 100 grains of Nitrate (*id est*, 1 of salt decomposes, nearly, 3 of Nitrate).

So again, in order to form the Iodide of Silver—what are about the proportions in which the two salts should be mixed? The equivalent of Iodide of Potassium is 166, and that of Nitrate of Silver is 170. These numbers so nearly correspond, that it is common to direct that *equal weights* of the two salts should be taken.

One more illustration will suffice. Supposing it is required to form 20 *grains* of Iodide of Silver—how much Iodide of Potassium and Nitrate of Silver must be used? One equivalent, or 166 parts, of Iodide of Potassium, will yield an equivalent, or 234 parts, of Iodide of Silver; therefore

as 234 : 166 : : 20 : 14·2.

Hence, if 14·2 grains of the Iodide of Potassium be dissolved in water, and 14·5 grains of the Nitrate of Silver added, the yellow precipitate, when washed and dried, will weigh precisely 20 grains.

H. ON THE ATOMIC THEORY.

The atomic theory, originally proposed by Dalton, so much facilitates the comprehension of chemical reactions generally, that it may be useful to give a short sketch of it before we proceed.

It is supposed that all matter is made up of an infinite number of minute atoms, which are elementary, and do not admit of further division. Each of these atoms possesses an actual weight, although inappreciable by our present methods of investigation. Simple atoms, by uniting with each other, form *compound atoms*, and when these compounds are broken up, the elementary constituent atoms are not destroyed, but separate from each other, in possession of all their original properties.

In representing the simple atomic structure of bodies, *circles* may be used, as in the following diagram.

Fig. 1. Fig. 2. Fig. 3.

Fig. 1 is a compound atom of Sulphuric Acid, consisting of an atom of Sulphur united intimately with three of Oxygen; fig. 2 is an atom of Peroxide of Nitrogen, NO_4; and fig. 3, an atom of Nitric Acid, composed of Nitrogen 1 atom, Oxygen 5 atoms, or in symbols NO_5.

The term "atomic weight" substituted for equivalent proportion.—If we suppose that the simple atoms of different kinds of matter *differ in weight*, and that this difference is expressed by their equivalent numbers, the whole laws of combination follow by the simplest reasoning. It is easy to understand that an atom of one element or compound would displace, or be substituted for, a single atom of another; therefore, taking as the illustration the decomposition of Iodide of Potassium by Chlorine, the weight of the latter element required to liberate 126 grains of Iodine is 36 grains, *because the weights of the atoms of those two elementary bodies are as* 36 *to* 126. So again, in the reaction between Chloride of Sodium and Nitrate of Silver, a compound atom of the former, represented by the weight 60, reacts upon a compound atom of the latter, which equals 170.

Therefore in place of the term "equivalent" or "combining proportion," it is more usual to employ that of "atomic weight." Thus the atomic weight of Oxygen is 8, represented by the symbol O; that of Sulphur is 16; hence the atomic weight of the compound atom of Sul-

phuric Acid, or SO_3, is necessarily equal to the combined weights of the four simple atoms; *id est*, 16+24=40.

I. ON THE CHEMISTRY OF ORGANIC SUBSTANCES.

By "organic" substances are meant those which have possessed *life*, with definite organs and tissues, in contradistinction to the various forms of dead inorganic matter, in which no structural organization of that kind is found. The term organic, however, is also applied to substances which are obtained by chemical processes from the vegetable and animal kingdom, although they cannot themselves be said to be living bodies; thus *Acetic Acid*, procured by the distillation of woody fibre, and Alcohol, by fermentation from Starch, are strictly organic substances.

The class of organic bodies embraces a great variety of products, which, like inorganic Oxides, may be divided into neutral, acid, and basic.

The organic *acids* are numerous, including Acetic Acid, Tartaric, Citric, and a variety of others.

The *neutral substances* cannot easily be assimilated to any class of inorganic compounds; as examples, take Starch, Sugar, Lignine, etc.

The *bases* are also a large class. They are mostly rare substances, not familiarly known: Morphia, obtained from Opium; Quinia, from Quinine; Nicotine, from Tobacco, are illustrations.

Composition of organic and inorganic bodies contrasted.—There are more than fifty elementary substances found in the inorganic kingdom, but only *four*, commonly speaking, in the organic: these four are Carbon, Hydrogen, Nitrogen, and Oxygen. Some organic bodies contain only Carbon and Hydrogen; many others—such as sugars, gum, alcohol, fats, vegetable acids—Carbon, Hydrogen, and Oxygen. The *Nitrogenous bodies*, so called, containing Nitrogen in addition to the other elements, are principally

substances derived from animal and vegetable tissues, such as Albumen, Fibrine, Gelatine, etc.; Sulphur and Phosphorus are also present in many of the Nitrogenous bodies, but only to a small extent.

Organic substances, although simple as regards the number of elements involved in their formation, are often highly complex in the arrangement of the atoms; this may be illustrated by the following formulæ:—

Starch	$C_{24}H_{20}O_{20}$
Lignine	$C_{24}H_{20}O_{20}$
Cane Sugar	$C_{24}H_{22}O_{22}$
Grape Sugar . . .	$C_{24}H_{28}O_{28}$

Inorganic bodies, as already shown, unite *in pairs*—two elements join to form a binary compound; two binary compounds produce a salt; two salts associated together form a double salt. With organic bodies however the arrangement is different—the elementary atoms are all grouped equally in one compound atom, which is highly complex in structure and cannot be split up into binary products.

Observe also, as characteristic of Organic Chemistry, the apparent similarity in composition between bodies which differ widely in properties. As examples, take *Lignine*, or cotton fibre, and *Starch*, each of which contains the three elements united as $C_{24}H_{20}O_{20}$.

Mode of distinguishing between organic and inorganic matter.—A simple means of doing this is as follows:—place the suspected substance upon a piece of platinum-foil, and heat it to redness with a spirit-lamp: if it first *blackens*, and then burns completely away, it is probably of organic origin. This test depends upon the fact, that the constituent elements of organic bodies are all either themselves volatile, or capable of forming volatile combinations with Oxygen. Inorganic substances, on the other

hand, are often unaffected by heat, or, if volatile, are dissipated without previous charring.

These remarks may be illustrated by the combustion of coal or wood in an ordinary furnace;—first, an escape of Carbon and Hydrogen, united in the form of volatile gaseous matter, takes place, leaving behind a black cinder, which consists of Carbon and inorganic matter combined; afterwards this Carbon burns away into Carbonic Acid, and a grey ash is left, which is composed of inorganic salts, and is indestructible by heat.

CHAPTER II.

VOCABULARY OF PHOTOGRAPHIC CHEMICALS.

ACETIC ACID.

Symbol, $C_4H_3O_3 + HO$. Atomic weight, 60.

Acetic Acid is a product of the *oxidation* of Alcohol. Spirituous liquids, when perfectly pure, are not affected by exposure to air; but if a portion of yeast, or *Nitrogenous organic matter* of any kind, is added, it soon acts as a *ferment*, and causes the spirit to unite with oxygen derived from the atmosphere, and so to become *sour* from formation of vinegar, or Acetic Acid, as it is properly termed.

The most concentrated Acetic Acid is obtained by neutralizing common vinegar with Carbonate of Soda and crystallizing out the Acetate of Soda so formed; this Acetate of Soda is then distilled with Sulphuric Acid, which removes the Soda and liberates Acetic Acid: the Acetic Acid being volatile, distils over, and may be condensed.

Properties of Acetic Acid.—The strongest acid contains only a single atom of water; it is sold under the name of "Glacial Acetic Acid," so called from its property of solidifying at a moderately low temperature. At about 50° the crystals melt, and form a limpid liquid of pungent

odour, and a density nearly corresponding to that of water. The specific gravity of Acetic Acid, however, is no test of its real strength, which can only be estimated by analysis.

In purchasing the commercial acid for Photographic purposes it is important to distinguish the *Glacial Acid* from a liquid of "ten per cent. real acid" sometimes sold; also it is well to test for the presence of *Sulphuric Acid*, which may be recognized by the white precipitate produced on adding a drop of solution of Chloride of Barium. (See Sulphuric Acid.)

ACETATE OF IRON. *See* IRON, ACETATE OF.

ACETATE OF SILVER. *See* SILVER, ACETATE OF.

ALBUMEN.

Albumen is an organic principle, found both in the animal and vegetable kingdom. In addition to the usual elements of organic bodies, viz. Carbon, Hydrogen, and Oxygen, it contains Nitrogen.

Properties of Albumen.—These are best studied in the *white of egg*, which is a very pure form of Albumen.

Albumen is capable of existing in two different states; in one of which it is soluble, in the other insoluble, in water. The aqueous solution of the soluble variety gives a slightly alkaline reaction to test-paper; it is somewhat thick and glutinous, but becomes more fluid on the addition of a small quantity of an alkali, such as Potash or Ammonia.

The coagulation of Albumen.—There are several means of converting the soluble variety of Albumen into the insoluble, or coagulated Albumen:-

1. *By the application of heat.*—A moderately strong solution of Albumen becomes opalescent and coagulates on being heated to about 150°, but a temperature of 212° is

required if the liquid is very dilute. A layer of *dried* Albumen cannot easily be coagulated by the mere application of heat.

2. *By addition of strong acids.*—Nitric Acid coagulates Albumen very perfectly without the aid of heat. Acetic Acid however does not coagulate Albumen, but appears to enter into combination with it, forming a compound soluble in warm water acidified by Acetic Acid.

3. *By the action of metallic salts.*—Many of the salts of the metals coagulate Albumen very perfectly. Nitrate of Silver does so; also the Bichloride of Mercury. The precipitate in these cases contains a portion of the base of the salt united with Albumen. The addition of an alkali like Ammonia to Nitrate of Silver prevents coagulation.

Chemical composition of Albumen.—Albumen belongs to the *Nitrogenous* class of organic substances (see page 328). It also contains small quantities of Sulphur and Phosphorus. The presence of the former element is shown in the blackening of silvered surfaces, or in the discoloration of Nitrate of Silver Baths, by albuminous solutions, which is due to a formation of *Sulphuret* of Silver.

ALCOHOL.

Symbol, $C_4H_6O_2$. Atomic weight, 46.

Alcohol is obtained by the careful distillation of any spirituous or fermented liquor. If wine or beer be placed in a retort, and heat applied, the Alcohol, being more volatile than water, rises first, and is condensed in an appropriate receiver; a portion of the vapour of water however passes over with the Alcohol, and dilutes it to a certain extent, forming what is termed "Spirits of Wine." Much of this water may be removed by redistillation from Carbonate of Potash, in the manner described at page 221 of this Work; but in order to render the Alcohol

thoroughly *anhydrous*, it is necessary to employ the *quicklime*, which possesses a still greater attraction for water. An equal weight of this powdered lime is mixed with the Alcohol, and the two are distilled together.

Properties of Alcohol.—Pure anhydrous Alcohol is a limpid liquid, of an agreeable odour and pungent taste; sp. gr. at 60° ·794. It absorbs vapour of water, and becomes diluted by exposure to damp air; boils at 173° Fahr. It has never been frozen.

Alcohol distilled from Carbonate of Potash has a sp. gr. of ·823, and contains 90 per cent. of real spirit.

The specific gravity of ordinary rectified Spirits of Wine is usually about ·840, and it contains 80 to 83 per cent. of absolute Alcohol.

AMMONIA.

Symbol, NH_3 or NH_4O. Atomic weight, 17 or 26.

The liquid known by this name is an aqueous solution of a volatile gas.

Ammoniacal gas contains 1 atom of Nitrogen combined with 3 of Hydrogen. These elementary bodies exhibit no affinity for each other, but they can be made to unite under certain circumstances, and the result is Ammonia.

Properties of Ammonia.—Ammoniacal gas is soluble in water to a large extent; the solution possesses those properties which are termed alkaline (see page 310). Ammonia however differs from the other alkalies in one important particular—it is volatile: hence the original colour of Turmeric-paper affected by Ammonia is restored on the application of heat. Solution of Ammonia absorbs Carbonic Acid rapidly from the air and is converted into Carbonate of Ammonia; it should therefore be preserved in stoppered bottles. Besides Carbonate, commercial Ammonia often contains Chloride of Ammonium, recognized by the white

precipitate given by Nitrate of Silver after acidifying with pure Nitric Acid.

The strength of commercial Ammonia varies greatly: that sold for pharmaceutical purposes, under the name of Liquor Ammoniæ, contains about 10 per cent. of real Ammonia. The sp. gr. of aqueous Ammonia diminishes with the proportion of Ammonia present, the Liquor Ammoniæ being usually about ·936.

Chemical Properties.—Ammonia, although forming a large class of salts, appears at first sight to contrast strongly in composition with the alkalies proper, such as Potash and Soda. Mineral bases generally are *protoxides of metals*, as already shown at page 310, but Ammonia consists simply of Nitrogen and Hydrogen united without Oxygen. The following remarks may perhaps tend somewhat to elucidate the difficulty.—

Theory of Ammonium.—This theory supposes that a substance exists possessing the properties of a metal, but differing from metallic bodies generally in being *compound* in structure: the formula assigned to it is NH_4; that is, 1 atom of Nitrogen united with 4 of Hydrogen. This hypothetical metal is termed "Ammonium," and Ammonia, associated with an atom of water, may be viewed as its *Oxide;* for $NH_3 + HO$ plainly equals NH_4O. The composition of the *salts* of Ammonia is in this view assimilated to those of the bases proper. Thus, Sulphate of Ammonia is a Sulphate of the Oxide of Ammonium; Muriate, or Hydrochlorate, of Ammonia is a Chloride of Ammonium, etc.

AQUA REGIA. *See* NITRO-HYDROCHLORIC ACID.

BICHLORIDE OF MERCURY.

See MERCURY, BICHLORIDE OF.

BROMINE.

Symbol, Br. Atomic weight, 78.

This elementary substance is obtained from the uncrystallizable residue of sea-water termed *bittern*. It exists in the water in very minute proportion, and combined with Magnesium, in the form of a soluble Bromide.

Properties.—Bromine is a deep reddish-brown liquid of a disagreeable odour, and fuming strongly at common temperatures; sparingly soluble in water (1 part in 23, Löwig), but more abundantly so in Alcohol, and especially in Ether. Specific gravity, 3·0.

Bromine is closely analogous to Chlorine and Iodine in its chemical properties. It stands on the list intermediately between the two; its affinities being stronger than those of Iodine, but weaker than Chlorine. (See Chlorine.)

BROMIDE OF POTASSIUM.

Symbol, KBr. Atomic weight, 118.

Bromide of Potassium is prepared by adding Bromine to Caustic Potash, and heating the product, which is a mixture of Bromide of Potassium and Bromate of Potash, to redness, in order to drive off the Oxygen from the latter salt. It crystallizes in anhydrous cubes like the Chloride, and Iodide, of Potassium; it is easily soluble in water, but more sparingly so in Alcohol; it yields red fumes of Bromine when acted upon by Sulphuric Acid.

BROMIDE OF SILVER. *See* SILVER, BROMIDE OF.

CARBONATE OF SODA.

Symbol, $NaO\,CO_2 + 10\,Aq.$

This salt was formerly obtained from the ashes of sea-

weeds, but is now more economically manufactured on a large scale from common salt. The Chloride of Sodium is first converted into Sulphate of Soda, and afterwards the Sulphate into Carbonate of Soda.

Properties.—The perfect crystals contain ten atoms of water, which are driven off by the application of heat, leaving a white powder—the anhydrous Carbonate. *Common washing Soda* is a neutral Carbonate, contaminated to a certain extent with Chloride of Sodium and Sulphate of Soda. The Carbonate used for effervescing draughts is either a Bicarbonate, with 1 atom of water, or a Sesquicarbonate, containing about 40 per cent. of real alkali (18 per cent. more than the crystals). Carbonate of Soda is soluble in twice its weight of water at 60°, the solution being strongly alkaline.

CARBONATE OF POTASH.

See POTASH, CARBONATE OF.

CHARCOAL, ANIMAL.

Animal Charcoal is obtained by heating animal substances, such as bones, dried blood, horns, etc. to redness, in close vessels, until all volatile empyreumatic matters have been driven off and a residue of Carbon remains. When prepared from bones it contains a large quantity of Inorganic matter in the shape of Carbonate and Phosphate of Lime, the former of which salts produces *alkalinity* in reacting upon Nitrate of Silver (see p. 105). Animal Charcoal is freed from these earthy salts by repeated digestion in Muriatic Acid, but unless very carefully washed it is apt to retain an acid reaction, and so to liberate free Nitric Acid when added to solution of Nitrate of Silver.

Properties.—Animal Charcoal, when pure, consists solely of Carbon, and burns away in the air without leaving any

residue: it is remarkable for its property of decolorizing solutions; the organic colouring substance being separated, but not actually *destroyed* as in the case of Chlorine employed as a bleaching agent. This power of absorbing colouring matter is not possessed in an equal degree by all varieties of Charcoal, but is in great measure peculiar to those derived from the animal kingdom.

CHINA CLAY, OR KAOLIN.

This is prepared, by careful levigation, from mouldering granite and other disintegrated felspathic rocks. It consists of the *Silicate of Alumina*—that is, of Silicic Acid, or Flint, which is an Oxide of Silicon, united with the base Alumina (Oxide of Aluminum). Kaolin is perfectly insoluble in water and acids, and produces no decomposition in solution of Nitrate of Silver. It is employed by Photographers to separate the finely divided Sulphuret of Silver which produces the black colour in Nitrate Baths which have been used with Albumen.

CHLORINE.

Symbol, Cl. Atomic weight, 36.

Chlorine is a chemical element found abundantly in nature, combined with metallic Sodium in the form of Chloride of Sodium, or Sea-salt.

Preparation.—By distilling common Salt with Sulphuric Acid, Sulphate of Soda and Hydrochloric Acid are formed. Hydrochloric Acid contains Chlorine combined with Hydrogen; by the action of *nascent* Oxygen (see Oxygen), the Hydrogen may be removed in the form of water, and the Chlorine left alone.

Properties. — Chlorine is a greenish-yellow gas, of a

pungent and suffocating odour; soluble to a considerable extent in water, the solution possessing the odour and colour of the gas. It is nearly 2½ times as heavy as a corresponding bulk of atmospheric air.

Chemical properties.—Chlorine belongs to a small natural group of elements which contains, besides itself, Bromine, Iodine, and Fluorine. They are characterized by having a strong affinity for Hydrogen, and also for the metals, but are comparatively indifferent to Oxygen. Many metallic substances actually undergo *combustion* when projected into an atmosphere of Chlorine, the union between the two taking place with extreme violence. The characteristic bleaching properties of Chlorine gas are explained in the same manner—Hydrogen is removed from the organic substance, and in that way the structure is broken up and the colour destroyed. Chlorine is more powerful in its affinities than either Bromine or Iodine. The salts formed by these three elements are closely analogous in composition and often in properties. Those of the Alkalies, Alkaline Earths, and many of the Metals are soluble in water, but the Silver salts are insoluble; the Lead salts sparingly so.

The combinations of Chlorine, Bromine, Iodine, and Fluorine, with Hydrogen, are acids, and neutralize Alkalies in the usual manner, with formation of Alkaline Chloride and water (see page 314).

The test by which the presence of Chlorine is detected, either free or in combination with bases, is *Nitrate of Silver;* it gives a white curdy precipitate of Chloride of Silver, insoluble in Nitric Acid, but soluble in Ammonia.

CHLORIDE OF AMMONIUM.

Symbol, NH_4Cl. Atomic weight, 54.

This salt, also known as Muriate or Hydrochlorate of

Ammonia, occurs in commerce in the form of colourless and translucent masses, which are procured by *sublimation*, the dry salt being volatile when strongly heated. It dissolves in an equal weight of boiling, or in three parts of cold, water. It contains more *Chlorine*, in proportion to the weight used, than Chloride of Sodium, the atomic weights of the two being as 54 to 60.

CHLORIDE OF BARIUM.

Symbol, $BaCl + 2\,HO$. Atomic weight, 123.

Barium is a metallic element, very closely allied to Calcium, the elementary basis of *Lime*. The Chloride of Barium is commonly employed as a test for Sulphuric Acid, with which it forms an insoluble precipitate of Sulphate of Baryta; also in preparing positive paper, as a substitute for Chloride of Sodium.

Properties of Chloride of Barium.—Chloride of Barium occurs in the form of white crystals, soluble in about two parts of water, at common temperatures. These crystals contain two atoms of water of crystallization, which are expelled at 212°, leaving the anhydrous Chloride.

CHLORIDE OF GOLD. *See* GOLD, CHLORIDE OF.

CHLORIDE OF SODIUM.

Symbol, NaCl. Atomic weight, 60.

Common Salt exists abundantly in nature, both in the form of solid rock-salt and dissolved in the waters of the ocean.

Properties of the pure Salt.—Fusible without decomposition at low redness, but sublimes at higher temperatures; the melted salt concretes into a hard white mass on cooling. Nearly insoluble in absolute alcohol, but dissolves in

minute quantity in rectified spirit. Soluble in three parts of water, both hot and cold. Crystallizes in cubes, which are anhydrous.

Impurities of common Salt.—Table salt often contains large quantities of the Chlorides of Magnesium and Calcium, which being deliquescent, produce a dampness by absorption of atmospheric moisture: also Sulphate of Soda is commonly present. The salt may be purified by repeated recrystallization, but it is more simple to prepare the pure compound directly, by neutralizing Hydrochloric Acid with Carbonate of Soda.

CHLORIDE OF SILVER. *See* SILVER, CHLORIDE OF.

CYANIDE OF POTASSIUM.

Symbol, K, C_2N, or KCy. Atomic weight, 66.

This salt is a compound of Cyanogen gas with the metal Potassium. Cyanogen is not an elementary body, like Chlorine or Iodine, but consists of Carbon and Nitrogen united in a peculiar manner. Although a compound substance, it reacts in the manner of an element, and is therefore (like *Ammonium*, previously described) an exception to the usual laws of chemistry, as given in the last chapter. Many other bodies of a similar character are known, but it is not necessary to allude to them at the present time.

Properties.—Commercial Cyanide of Potassium is ordinarily contaminated with a large percentage of Carbonate of Potash, from which it may be freed by boiling in Alcohol; the spirituous solution on cooling deposits small crystals, which are deliquescent, alkaline to test-paper, and evolve an odour of Prussic Acid on exposure to the air. Cyanide of Potassium is freely soluble in water, but the solution eventually decomposes into Prussic Acid (Cyanide of Hydrogen) and Potash. It is highly poisonous.

ETHER.

Symbol, C_4H_5O. Atomic weight, 37.

Ether is obtained by distilling a mixture of Sulphuric Acid and Alcohol. If the formula of Alcohol ($C_4H_6O_2$) be compared with that of Ether, it will be seen to differ from it in the possession of an additional atom of Hydrogen and of Oxygen;—in the reaction the Sulphuric Acid removes these elements in the form of *water*, and by so doing converts one atom of Alcohol into an atom of Ether. The term *Sulphuric* applied to the commercial Ether has reference only to the manner of its formation.

Properties of Ether.—The properties of Ether have been described to some extent at page 219. The following particulars however may be added. It is neither acid nor alkaline to test-paper. Specific gravity at 60°, about ·720. Boils at 98° Fahrenheit. The vapour is exceedingly dense, and may be seen passing off from the liquid and falling to the ground: hence the danger of pouring Ether from one bottle to another if a flame be near at hand.

Ether does not mix with water in all proportions; hence if the two are shaken together, after a short time the former rises and floats upon the surface. In this way a mixture of Ether and Alcohol may be separated from each other, as in the common process of *washing* Ether. The water employed however always retains a certain portion of Ether (about a tenth part of its bulk), and acquires a strong ethereal odour; washed Ether also contains water in small proportion.

Bromine and Iodine are both soluble in Ether and gradually react upon and decompose it. (See page 100.)

The strong alkalies, such as Potash and Soda, also decompose Ether slightly after a time, but not immediately (see page 220). Exposed to air and light, Ether is oxidized and acquires a peculiar odour (see page 99).

Ether dissolves fatty and resinous substances readily, but inorganic salts are mostly insoluble in this fluid. Hence it is that Iodide of Potassium and other substances dissolved in Alcohol are precipitated to a certain extent by the addition of Ether.

FLUORIDE OF POTASSIUM.

Symbol, KF. Atomic weight, 59.

Preparation.—Fluoride of Potassium is formed by saturating Hydrofluoric Acid with Potash, and evaporating to dryness in a platinum vessel. *Hydrofluoric Acid* contains Fluorine combined with Hydrogen; it is a powerfully acid and corrosive liquid, formed by decomposing Fluor Spar, which is a *Fluoride of Calcium*, with strong Sulphuric Acid, the action which takes place being precisely analogous to that involved in the preparation of Hydrochloric Acid, which see.

Properties.—A deliquescent salt, occurring in small and imperfect crystals. Very soluble in water; the solution acts upon glass in the same manner as Hydrofluoric Acid.

FORMIC ACID.

Symbol, C_2HO_3. Atomic weight, 37.

This substance was originally discovered in the *red ant* (*Formica rufa*), but it is prepared on a large scale by distilling *Starch* with Binoxide of Manganese and Sulphuric Acid.

Properties.—The strength of commercial Formic Acid is uncertain, but it is always more or less dilute. The strongest acid, as obtained by distilling Formiate of Soda with Sulphuric Acid, is a fuming liquid with a pungent odour, and containing only one atom of water; it inflames the skin in the same manner as the sting of the ant.

Formic Acid reduces the Oxides of Gold, Silver, and Mercury, to the metallic state, and is itself oxidized into Carbonic Acid. The alkaline formiates also possess the same properties.

GALLIC ACID.

Symbol, $C_7H_3O_5 + HO$. Atomic weight, 94.

The chemistry of Gallic Acid is described at page 39: to the particulars there given the following may be added. Gallic Acid is soluble in 100 parts of cold and in 3 of boiling water; readily soluble in Alcohol, but sparingly so in Ether. The aqueous solution of Gallic Acid is prone to decomposition on keeping. It is stated that the addition of *Acetic Acid*, in the proportion of a drachm of the Glacial Acid to 12 ounces of the saturated solution, prevents this in great measure; also that a drop or two of Oil of Cloves produces the same effect.

GELATINE.

Symbol, $C_{13}H_{10}O_5N_2$. Atomic weight, 156.

This is an organic substance somewhat analogous to Albumen, but differing from it in properties. It is obtained by subjecting bones, hoofs, horns, calves' feet, etc. to the action of boiling water. The jelly formed on cooling is termed *size*, or when dried and cut into slices, *glue*. Gelatine, as it is sold in the shops, is a pure form of Glue. *Isinglass* is Gelatine prepared, chiefly in Russia, from the air-bladders of certain species of sturgeon.

Properties of Gelatine.—Gelatine softens and swells up in cold water, but scarcely *dissolves* until heated: the hot solution, on cooling, forms a tremulous jelly. One ounce of cold water will retain about 3 grains of Isinglass

without gelatinizing; but much depends upon the temperature, a few degrees greatly affecting the result.

Gelatine does not form any compound with Oxide of Silver in the manner of Albumen, which fact no doubt explains the difference in their photographic action.

GOLD, CHLORIDE OF.

Symbol, $AuCl_3$. Atomic weight, 308.

This salt is formed by dissolving metallic Gold in Nitro-hydrochloric Acid or Aqua regia, and evaporating at a gentle heat. The solution affords deliquescent crystals of a deep orange-colour.

Properties.—The solution of Perchloride of Gold is of a bright yellow colour when dilute, but nearly red if concentrated. As usually sold, it contains an excess of Hydrochloric Acid; but even if freed from this, it is still acid to test-paper, although neutral, chemically speaking. It is decomposed with precipitation of metallic Gold by Charcoal, Sulphurous Acid, and many of the vegetable acids; also by Protosulphate and Protonitrate of Iron. It tinges the cuticle of an indelible purple tint. It is soluble in Alcohol and also in Ether.

The addition of *Ammonia* to Perchloride of Gold produces the dangerous explosive compound known as "Fulminating Gold."

GOLD, HYPOSULPHITE OF.

Symbol, $AuO\,S_2O_2$. Atomic weight, 256.

Hyposulphite of Gold is produced by the reaction of Chloride of Gold upon Hyposulphite of Soda. (See page 166.)

The salt sold in commerce as Sel d'Or, is a double Hy-

posulphite of Gold and Soda, containing one atom of the former salt to three of the latter, with four atoms of water of crystallization.

Hyposulphite of Gold is an excessively unstable substance, and cannot exist in an isolated state. The double salt with Soda, although more permanent, is nevertheless easily decomposed. The addition of Hyposulphite of Soda to *excess of Chloride of Gold*, produces free Sulphurous Acid and a reduction of metallic Gold, as shown at page 285.

GRAPE SUGAR.

Symbol, $C_{24}H_{28}O_{28}$. Atomic weight, 396.

This modification of Sugar, often termed "Granular Sugar," or "Glucose," exists abundantly in the juice of grapes, and also in many other varieties of fruits. It forms the saccharine concretion found in honey, raisins, dried figs, etc. It may be produced artificially by the action of fermenting principles, and of dilute mineral acids, upon Starch.

Properties.—Grape Sugar crystallizes slowly and with difficulty from a concentrated aqueous solution, in small hemispherical nodules, which are hard, and feel gritty between the teeth. It is much less sweet to the taste than Cane Sugar, and not so soluble in water (1 part dissolves in $1\frac{1}{2}$ of cold water). Grape Sugar tends to absorb oxygen, and hence it possesses the property of decomposing the salts of the noble metals, and reducing them by degrees to the metallic state, even without the aid of light. The action however in the case of *Nitrate of Silver* is slow, unless the temperature is somewhat elevated. *Cane* Sugar does not possess these properties to an equal extent, and hence it is readily distinguished from the other variety.

HONEY.

This substance contains two distinct kinds of Sugar, —the Grape Sugar, and an uncrystallizable substance analogous to, or identical with, the Treacle found associated with common Sugar in the cane-juice. The agreeable taste of Honey probably depends upon the latter, but its reducing power on metallic oxides is due to the former. Pure Grape Sugar can readily be obtained from inspissated Honey, by treating it with Alcohol, which dissolves out the syrup, but leaves the crystalline portion.

HYDROCHLORIC ACID.

Symbol, HCl. Atomic weight, 37.

Hydrochloric Acid is a volatile gas, which may be liberated from the salts termed Chlorides by the action of Sulphuric Acid. The acid, by its superior affinities, removes the base; thus,—

$$NaCl + HO\,SO_3 = NaO\,SO_3 + HCl.$$

Properties.—Abundantly soluble in water, forming the liquid Hydrochloric or Muriatic Acid of commerce. The most concentrated solution of Hydrochloric Acid has a sp. gr. 1·2, and contains about 40 per cent. of gas; that commonly sold is somewhat weaker, sp. gr. 1·14 = 28 per cent. real acid.

Pure Hydrochloric Acid is colourless, and fumes in the air. The yellow colour of the commercial acid depends upon the presence of traces of Perchloride of Iron or organic matter; commercial Muriatic Acid also often contains a portion of free Chlorine and of Sulphuric Acid.

Muriatic Acid is employed by the Photographer in the preparation of Aqua regia, used for dissolving Gold, and

also in producing the yellow Perchloride of Iron. The common Acid, sold at a low price, answers sufficiently well for both purposes.

HYDRIODIC ACID.

Symbol, HI. Atomic weight, 127.

This is a gaseous compound of Hydrogen and Iodine, corresponding in composition to the Hydrochloric Acid. It cannot however, from its instability, be obtained in the same manner, since, on distilling an Iodide with Sulphuric Acid, the Hydriodic Acid first formed is subsequently decomposed into Iodine and Hydrogen. An aqueous solution of Hydriodic Acid is easily prepared by adding Iodine to water containing Sulphuretted Hydrogen gas; a decomposition takes place, and Sulphur is set free: thus, $HS + I = HI + S$.

Properties.—Hydriodic Acid is very soluble in water, and yields a strongly acid liquid. The solution, colourless at first, soon becomes brown from decomposition, and liberation of free Iodine. It may be restored to its original condition by adding solution of Sulphuretted Hydrogen.

HYDROSULPHURIC ACID.

Symbol, HS. Atomic weight, 17.

This substance, also known as Sulphuretted Hydrogen, is a gaseous compound of Sulphur and Hydrogen, analogous in composition to Hydrochloric and Hydriodic Acids. It is usually prepared by the action of dilute Sulphuric Acid upon Sulphuret of Iron, as described at page 375; the decomposition which ensues under these circumstances is similar to that involved in the preparation of the Hydrogen acids generally:—

$$FeS + HO\,SO_3 = FeO\,SO_3 + HS.$$

Properties.—Cold water absorbs three times its bulk of Hydrosulphuric Acid, and acquires the peculiar putrid odour and poisonous qualities of the gas. The solution is faintly acid to test-paper, and becomes opalescent on keeping, from gradual separation of Sulphur. It is decomposed by Nitric Acid, and also by Chlorine and Iodine. It precipitates Silver from its solutions, in the form of black Sulphuret of Silver, also Copper, Mercury, Lead, etc.; but Iron and other metals of that class are not affected if the liquid contains free acid. Hydrosulphuric Acid is constantly employed in the chemical laboratory for these and other purposes.

HYDROSULPHATE OF AMMONIA.

Symbol, $NH_4S\,HS$. Atomic weight, 51.

The liquid known by this name, and formed by passing Sulphuretted Hydrogen gas into Ammonia, is a double Sulphuret of Hydrogen and Ammonium. In the preparation, the passage of the gas is to be continued until the solution gives no precipitate with Sulphate of Magnesia and smells strongly of Hydrosulphuric Acid.

Properties.—Colourless at first, but afterwards changes to yellow from liberation and subsequent solution of Sulphur. Becomes milky on the addition of any acid. Precipitates, in the form of Sulphuret, all the metals which are affected by Sulphuretted Hydrogen, and, in addition, those of the class to which Iron, Zinc, and Manganese belong.

Hydrosulphate of Ammonia is employed occasionally to darken the Negative Photographic image, and also in the preparation of Iodide of Ammonium; the separation of Silver from Hyposulphite solutions, etc.

HYPOSULPHITE OF SODA.

Symbol, NaO S_2O_2 + 5 HO. Atomic weight, 125.

The chemistry of Hyposulphurous Acid and the Hyposulphite of Soda has been sufficiently described at pages 53 and 161 of the present Work. The crystallized salt includes five atoms of water of crystallization, and has an atomic weight of 125.

HYPOSULPHITE OF GOLD. *See* GOLD, HYPOSULPHITE OF.

HYPOSULPHITE OF SILVER. *See* SILVER, HYPOSULPHITE OF.

IODINE.

Symbol, I. Atomic weight, 126.

Iodine is chiefly prepared at Glasgow, from *kelp*, which is the fused ash obtained by burning sea-weeds. The waters of the ocean contain minute quantities of the Iodides of Sodium and Magnesium, which are separated and stored up by the growing tissues of the marine plant.

In the preparation, the mother-liquor of kelp is evaporated to dryness and distilled with Sulphuric Acid; the Hydriodic Acid thus formed is decomposed by the high temperature, and fumes of Iodine condense in the form of opaque crystals.

Properties.—Iodine is met with in the shops in two forms,—the commercial and the resublimed Iodine. The former, which is sold at a lower price than the other, is sufficiently pure for most purposes.

Iodine has a bluish-black colour and metallic lustre; it stains the skin yellow, and has a pungent smell, like diluted Chlorine. It is extremely volatile when moist, boils at 350°, and produces dense violet-coloured fumes, which

condense in brilliant plates. Sp. gr. 4·946. Iodine is very sparingly soluble in water, 1 part requiring 7000 parts for perfect solution: even this minute quantity however tinges the liquid of a brown colour. Alcohol and Ether dissolve it more abundantly, forming dark-brown solutions. Iodine also dissolves freely in solutions of the alkaline Iodides; such as the Iodide of Potassium, of Sodium, and of Ammonium.

Chemical Properties.—Iodine belongs to the Chlorine group of elements, characterized by forming acids with Hydrogen, and combining extensively with the metals (see Chlorine). They are however comparatively indifferent to Oxygen, and also to each other. The Iodides of the alkalies, and alkaline earths (see page 308) are soluble in water; also those of Iron, Zinc, Cadmium, etc. The Iodides of Lead, Silver, and Mercury are nearly or quite insoluble.

Iodine possesses the property of forming a compound of a deep blue colour with Starch. In using this as a test, it is necessary first to liberate the Iodine (if in combination), by means of Chlorine, or Nitric Acid saturated with Peroxide of Nitrogen. The presence of Alcohol or Ether interferes to a certain extent with the result. (See page 99.)

IODIDE OF AMMONIUM.

Symbol, NH_4I. Atomic weight, 144.

The preparation and properties of this salt are described at page 223, to which the reader is referred.

IODIDE OF CADMIUM.

Symbol, CdI. Atomic weight, 182.

This salt is formed by heating filings of metallic Cad-

mium with Iodine, or by mixing the two together in a moist state. It is very soluble in water and Alcohol, the solution yielding large six-sided tables of a pearly lustre, which are permanent, and do not deliquesce by exposure. The Ethereal solution of Iodide of Cadmium does not appear to decompose with the same readiness as the other Iodides employed in the manufacture of Collodion. (See page 100.)

IODIDE OF IRON.

Symbol, FeI. Atomic weight, 154.

Iodide of Iron is prepared by digesting an excess of Iron filings with solution of Iodine. (See page 224.) It is very soluble in water and Alcohol, but the solution rapidly absorbs Oxygen and deposits Peroxide of Iron; hence the importance of preserving it in contact with metallic Iron, with which the separated Iodine may recombine. By very careful evaporation, hydrated crystals of Protoiodide may be obtained, but the composition of the solid salt usually sold under that name cannot be depended on.

The *Periodide* of Iron, corresponding to the *Perchloride*, has not been examined, and it is even doubtful if such a compound exists.

IODIDE OF POTASSIUM.

Symbol, KI. Atomic weight, 166.

This salt is usually formed by dissolving Iodine in solution of Potash until it begins to acquire a brown colour; a mixture of Iodide of Potassium and *Iodate of Potash* is thus formed; but by evaporation and heating to redness, the latter salt parts with its Oxygen, and is converted into Iodide of Potassium.

Properties.—It forms cubic and prismatic crystals, which should be hard, and *very slightly or not at all deliquescent.* Soluble in less than an equal weight of water at 60°; it is also soluble in Alcohol, but not in Ether. The proportion of Iodide of Potassium contained in a saturated alcoholic solution, varies with the strength of the spirit,—with common Spirits of Wine, sp. gr. ·836, it would be about 8 grains to the drachm; with Alcohol rectified from Carbonate of Potash, sp. gr. ·823, 4 or 5 grains; with absolute Alcohol, 1 to 2 grains. The solution of Iodide of Potassium is instantly coloured brown by free Chlorine (page 315); also very rapidly by Peroxide of Nitrogen (page 99): ordinary acids however act less quickly, Hydriodic Acid being first formed, and subsequently decomposed.

The impurities of commercial Iodide of Potassium, with the means to be adopted for their removal, are fully given at page 222.

IODIDE OF SILVER. *See* SILVER, IODIDE OF.

IRON, PROTOACETATE OF.

Symbol, $FeO\ C_4H_3O_3$. Atomic weight, 87.

There are two Acetates of Iron, both of which are readily soluble in water,—a Protoacetate, the solution of which is colourless, or nearly so, and a red Peracetate. The former, which corresponds in composition and properties to the Protosulphate and Protonitrate of Iron, may be obtained by mixing Acetate of Lead and Sulphate of Iron in atomic proportions. For a solution to contain 10 grains to the ounce, 16 grains of Sulphate of Iron and 21 grains of Acetate of Lead, each dissolved in four drachms of *cold* water, will be required.

IRON, PROTOSULPHATE OF.

Symbol, $FeO\ SO_3 + 7\ HO$. Atomic weight, 139.

The properties of this salt, and also of the two salifiable Oxides of Iron, are described at page 41. The following particulars may be added. The crystals of Protosulphate of Iron usually include 7 atoms of water, 6 of which are expelled at a temperature of 238° Fahr.; the salt effloresces, to a certain extent, by exposure to dry air,—losing water, and becoming white and powdery on the surface. Crystallized Sulphate of Iron dissolves in rather more than an equal weight of cold water, or in less of boiling water.

Aqueous solution of Sulphate of Iron absorbs the *Binoxide of Nitrogen*, acquiring a deep olive-brown colour: as this gaseous Binoxide is itself a reducing agent, the liquid so formed has been proposed as a more energetic developer than the Sulphate of Iron alone.

IRON, PROTONITRATE OF.

Symbol, $FeO\ NO_5 + 7\ HO$. Atomic weight, 153.

This salt, by careful evaporation *in vacuo* over Sulphuric Acid, forms transparent crystals, of a light green colour, and containing 7 atoms of water, like the Protosulphate. It is exceedingly unstable, and soon becomes red from decomposition, unless preserved from contact with air. The preparation of solution of Protonitrate of Iron, employed for developing Collodion Positives, is given at page 230.

IRON, PERCHLORIDE OF.

Symbol, Fe_2Cl_3. Atomic weight, 164.

There are two Chlorides of Iron, corresponding in com-

position to the Protoxide and the Sesquioxide respectively. The Protochloride is very soluble in water, forming a green solution, which precipitates a dirty white Protoxide on the addition of an alkali.

The Perchloride, as produced by dissolving the Sesquioxide of Iron in Hydrochloric Acid, is dark brown, and gives a foxy-red precipitate with the alkalies.

Perchloride of Iron may also be obtained in the solid form by heating Iron wire in excess of Chlorine; it condenses in the shape of brilliant and iridescent brown crystals, which are volatile, and dissolve in water, the solution being acid to test-paper. It is also soluble in Alcohol, forming the Tinctura Ferri Sesquichloridi of the Pharmacopœia. Commercial Perchloride of Iron ordinarily contains an excess of Hydrochloric Acid.

LITMUS.

Litmus is a vegetable substance, prepared from various *lichens*, which are principally collected on rocks adjoining the sea. The colouring matter is extracted by a peculiar process, and afterwards made up into a paste with chalk, plaster of Paris, etc.

Litmus occurs in commerce in the form of small cubes, of a fine violet-colour. In using it for the preparation of test-papers, it is digested in hot water, and sheets of porous paper are soaked in the blue liquid so formed. The red papers are prepared in a similar manner, and afterwards placed in water which has been rendered faintly acid with Sulphuric or Hydrochloric Acid.

MERCURY, BICHLORIDE OF.

Symbol, $HgCl_2$. Atomic weight, 274.

This salt, also called Corrosive Sublimate, and some-

times *Chloride of Mercury* (the atomic weight of Mercury being halved), may be formed by heating Mercury in excess of Chlorine, or, more economically, by subliming a mixture of Persulphate of Mercury and Chloride of Sodium.

Properties.—A very corrosive and poisonous salt, usually sold in semi-transparent, crystalline masses, or in the state of powder. Soluble in 16 parts of cold, and in 3 of hot water; more abundantly so in Alcohol, and also in Ether. The solubility in water may be increased almost to any extent by the addition of free Hydrochloric Acid.

The Protochloride of Mercury is an insoluble white powder, familiarly known under the name of *Calomel.*

NITRIC ACID.

Symbol, NO_5. Atomic weight, 54.

Nitric Acid, or "Aqua-fortis," is prepared by adding Sulphuric Acid to Nitrate of Potash, and distilling the mixture in a retort. Sulphate of Potash and free Nitric Acid are formed, the latter of which being volatile, distils over in combination with one atom of water previously united with the Sulphuric Acid.

Properties.—Anhydrous Nitric Acid is a solid substance, white and crystalline, but it cannot be prepared except by a most expensive and complicated process.

The concentrated *liquid* Nitric Acid contains 1 atom of water, and has a sp. gr. of about 1·5; if perfectly pure it is colourless, but usually it has a slight yellow tint, from partial decomposition into Peroxide of Nitrogen: it fumes strongly in the air.

The strength of commercial Nitric Acid is subject to much variation. An acid of sp. gr. 1·42, containing about 4 atoms of water, is commonly met with. If the specific gravity is lower than this, it will scarcely be adapted

for the preparation of Pyroxyline. The yellow *Nitrous Acid*, so called, is a strong Nitric Acid which is partially saturated with the brown vapours of Peroxide of Nitrogen; it has a high specific gravity, but this is somewhat deceptive, being caused in part by the presence of the Peroxide. On mixing with Sulphuric Acid the colour disappears, a compound being formed which has been termed a *Sulphate of Nitrous Acid*.

In the Appendix a Table is given which exhibits the quantity of real anhydrous Nitric Acid contained in samples of different densities.

Chemical Properties.—Nitric Acid is a powerful oxidizing agent (see page 15); it dissolves all the common metals, with the exception of Gold and Platinum. Animal substances, such as the cuticle, nails, etc., are tinged of a permanent yellow colour, and deeply corroded by a prolonged application. Nitric Acid forms a numerous class of salts, *all of which are soluble in water*. Hence its presence cannot be determined by any precipitating reagent, in the same manner as that of Hydrochloric and Sulphuric Acids.

Impurities of Commercial Nitric Acid.—These are principally *Chlorine* and *Sulphuric Acid;* also Peroxide of Nitrogen, which tinges the acid yellow, as already described. Chlorine is detected by diluting the acid with an equal bulk of distilled water, and adding a few drops of Nitrate of Silver,—*a milkiness*, which is due to Chloride of Silver in suspension, indicates the presence of Chlorine. In testing for Sulphuric Acid, dilute the Nitric Acid as before, and drop in a single drop of solution of Chloride of Barium; if Sulphuric Acid is present, an insoluble precipitate of Sulphate of Baryta will be formed.

NITROUS ACID. *See* SILVER, NITRITE OF.

NITRATE OF POTASH.

Symbol, $KO\,NO_5$. Atomic weight, 102.

This salt, also termed *Nitre* or *Saltpetre*, is an abundant natural product found effloresced upon the soil in certain parts of the East Indies. It is also produced artificially in what are called Nitre-beds.

The properties of Nitrate of Potash are described as far as is necessary at pages 213 and 214.

NITRATE OF BARYTA.

Symbol, $BaO\,NO_5$. Atomic weight, 131.

Nitrate of Baryta forms octahedral crystals, which are anhydrous. It is considerably less soluble than the Chloride of Barium, requiring 12 parts of cold and 4 of boiling water for solution. It may be substituted for the Nitrate of Lead in the preparation of Protonitrate of Iron.

NITRATE OF MAGNESIA.

Symbol, $MgO\,NO_5 + 6\,HO$. Atomic weight, 128.

Nitrate of Magnesia may be prepared by dissolving Carbonate of Magnesia in Nitric Acid. It crystallizes with difficulty in rhomboidal prisms, which are deliquescent and soluble in an equal weight of water. When intensely heated, it loses both water and acid, and Magnesia remains. For the impurities of the commercial salt, which render it unfit for Photographic use, see page 300.

NITRATE OF LEAD.

Symbol, $PbO\,NO_5$. Atomic weight, 166.

Nitrate of Lead is obtained by dissolving the metal, or

the Oxide of Lead, in *excess* of Nitric Acid, diluted with 2 parts of water. It crystallizes on evaporation in white anhydrous tetrahedra and octahedra, which are hard, and decrepitate on being heated; they are soluble in 8 parts of water at 60°.

Nitrate of Lead forms with Sulphuric Acid, or soluble Sulphates, a white precipitate, which is the insoluble Sulphate of Lead. The *Iodide* of Lead is also very sparingly soluble in water.

NITRATE OF SILVER.

See SILVER, NITRATE OF.

NITRO-HYDROCHLORIC ACID.

Symbol, $NO_4 + Cl$.

This liquid is the Aqua-regia of the old alchemists. It is produced by mixing together Nitric and Hydrochloric Acids: the Oxygen contained in the former combines with the Hydrogen of the latter, forming water and liberating Chlorine, thus:—

$$NO_5 + HCl = NO_4 + HO + Cl.$$

The presence of free Chlorine confers on the mixture the power of dissolving Gold and Platinum, which neither of the two acids possessed separately. In preparing Aqua-regia it is usual to mix one part, by measure, of Nitric Acid with four of Hydrochloric Acid, and to dilute with an equal bulk of water. The application of a gentle heat assists the solution of the metal; but if the temperature rises to the boiling point, a violent effervescence and escape of Chlorine takes place.

NITRO-SULPHURIC ACID.

For the chemistry of this acid liquid, see pages 86 and 209.

OXYGEN.

Symbol, O. Atomic weight, 8.

Oxygen gas may be obtained by heating Nitrate of Potash to redness, but in that case it is contaminated with a portion of Nitrogen. The salt termed Chlorate of Potash (the composition of which is closely analogous to that of the Nitrate, Chlorine being substituted for Nitrogen) yields abundance of pure Oxygen gas on the application of heat, and leaves behind Chloride of Potassium.

Chemical Properties.—Oxygen combines eagerly with many of the chemical elements, forming Oxides. This chemical affinity however is not well seen when the elementary body is exposed to the action of *Oxygen in the gaseous form*. It is the *nascent* Oxygen which acts most powerfully as an oxidizer. By nascent Oxygen is meant Oxygen on the point of separation from other elementary atoms with which it was previously associated; it may then be considered to be in the liquid form, and hence it comes more perfectly into contact with the particles of the body to be oxidized.

Illustrations of the superior chemical energy of nascent Oxygen are numerous, but none perhaps are more striking than the mild and gradual oxidizing influence exerted by atmospheric air, as compared with the violent action of Nitric Acid and bodies of that class which contain Oxygen loosely combined.

POTASH.

Symbol, KO + HO. Atomic weight, 57.

Potash is obtained by separating the Carbonic Acid from Carbonate of Potash by means of Caustic Lime. Lime is a more feeble base than Potash, but the Carbonate of Lime, being *insoluble* in water, is at once formed on

adding Milk of Lime to solution of Carbonate of Potash. (See page 317.)

Properties.—Usually met with in the form of solid lumps, or in cylindrical sticks, which are formed by melting the Potash and running it into a mould. It always contains one atom of water, which cannot be driven off by the application of heat.

Potash is soluble almost to any extent in water, much heat being evolved. The solution is powerfully alkaline (see page 310), and acts rapidly upon the skin; it dissolves fatty and resinous bodies, converting them into soaps. Solution of Potash absorbs Carbonic Acid quickly from the air, and should therefore be preserved in stoppered bottles; the glass stoppers must be wiped occasionally, in order to prevent them from becoming immovably fixed by the solvent action of the Potash upon the Silica of the glass.

The Liquor Potassæ of the London Pharmacopœia has a sp. gr. of 1·063, and contains about 5 per cent. of real Potash. It is usually contaminated with *Carbonate* of Potash, which causes it to effervesce on the addition of acids; also, to a less extent, with Sulphate of Potash, Chloride of Potassium, Silica, etc.

POTASH, CARBONATE OF.

Symbol, $KO\,CO_2$. Atomic weight, 70.

The impure Carbonate of Potash, termed *Pearlash*, is obtained from the ashes of wood and vegetable matter, in the same manner as Carbonate of Soda is prepared from the ashes of sea-weeds. Salts of Potash and of Soda appear essential to vegetation, and hence they are absorbed and appropriated by the living tissues of the plant. They exist in the vegetable structure, combined with organic acids, in the form of salts, like the Oxalate, Tartrate, etc., which when burned are converted into Carbonates.

Properties.—The Pearlash of commerce contains large and variable quantities of Chloride of Potassium, Sulphate of Potash, etc. A purer Carbonate is sold, which is free from Sulphates, and with only a trace of Chlorides. Carbonate of Potash is a strongly alkaline salt, deliquescent, and soluble in twice its weight of cold water; insoluble in Alcohol, and employed to deprive it of water. (See page 221.)

POTASH, BICARBONATE OF.

Symbol, $KO\,CO_2 + HO\,CO_2$. Atomic weight, 101.

This is formed by passing a stream of Carbonic Acid gas into a solution of the neutral Carbonate. It crystallizes nicely in large hydrated prisms, which are not deliquescent, and are more easily freed from impurities than the Protocarbonate of Potash.

PYROGALLIC ACID.

Symbol, $C_8H_4O_4$ (Stenhouse). Atomic weight, 84.

The chemistry of Pyrogallic Acid has been sketched at page 39. The following particulars may be added. It is soluble in Ether and Alcohol as well as in water; the aqueous solution blackens on exposure to the air, and deposits a brown powder; it gives a deep Indigo blue colour with Protosulphate of Iron, which changes to dark green if Peroxide be present. The addition of caustic alkalies decomposes Pyrogallic Acid, at the same time increasing the attraction for Oxygen: hence a mixture of Potash and Pyrogallic Acid is often employed for absorbing the Oxygen contained in atmospheric air.

SEL D'OR. *See* GOLD, HYPOSULPHITE OF.

SILVER, OXIDE OF.

Symbol, AgO. Atomic weight, 116.

Oxide of Silver is an olive-brown powder, obtained by adding a strong base, such as Potash, to Nitrate of Silver (page 316). It is soluble to a very minute extent in pure water, the solution possessing an alkaline reaction. Long exposure to light converts it into a black substance, which is either Suboxide or pure Silver. It is soluble in Hyposulphite of Soda and Cyanide of Potassium, also in Ammonia, and in Nitrate of Ammonia. It is used in staining glass of a yellow colour.

A *suboxide* of Silver has been described, having the formula Ag_2O, and obtained by exposing an ammoniacal solution of Protoxide to the action of air; it separates in the form of a brilliant grey film.

SILVER, CHLORIDE OF.

Symbol, AgCl. Atomic weight, 144.

The preparation and properties of Chloride of Silver are given at pages 17 and 21. The following particulars may be added:—it dissolves very sparingly in concentrated Hydrochloric Acid, but is absolutely insoluble in Nitric Acid.

The dry Chloride of Silver, heated to dull redness, fuses, and concretes on cooling into a grey semi-transparent substance, which has been termed *Horn Silver*, or *Luna cornea*.

Chloride of Silver may be reduced to the metallic state by fusing it with Potash, Soda, or their Carbonates; also by boiling it in a solution of Caustic Potash to which Sugar has been added. A third process is, by the action of metallic Zinc or Iron upon the moist salt acidified by Sulphuric Acid. (See page 376).

A *Subchloride* of Silver has been described, although not minutely. It is formed by the action of Hydrochloric Acid upon the Suboxide, and is insoluble in Nitric Acid, and less soluble in Ammonia than the Protochloride.

SILVER, BROMIDE OF.

Symbol, AgBr. Atomic weight, 186.

Is a yellowish insoluble powder, formed by the action of Bromine, or the Bromides, upon Nitrate of Silver. It dissolves in strong solution of Ammonia, also in Bromide or Iodide of Potassium or Ammonium, and in Chloride of Ammonium.

SILVER, IODIDE OF.

Symbol, AgI. Atomic weight, 234.

This salt may be prepared in the same manner as the Bromide and Chloride. It is of a yellow colour if *excess of Nitrate of Silver* is used in the precipitation, but more pale if the alkaline Iodide be in excess. Insoluble in water and in Nitric Acid; nearly but not perfectly so in Ammonia; also less easily dissolved by alkaline Chlorides and Hyposulphites than either of the corresponding Silver salts containing Chlorine and Bromine.

SILVER, FLUORIDE OF.

Symbol, AgF. Atomic weight, 127.

This compound differs from those just described in being soluble in water. The dry salt fuses on being heated, and is reduced by a higher temperature, and also on exposure to light.

SILVER, BROMO-IODIDE OF.

The name *Bromo-Iodide of Silver* has been given to the compound formed by acting upon metallic Silver with the vapours of Iodine and Bromine successively; also to the mixed salt obtained by decomposing Bromide and Iodide of Potassium, in the proper atomic proportions, by Nitrate of Silver. A third process sometimes followed for obtaining the Bromo-Iodide of Silver, viz. by the addition of *water* to a solution of Bromide and Iodide of Silver in Iodide of Potassium, appears to be founded upon wrong data, since there are good reasons for supposing that the whole of the Bromine, in that case, remains in solution, combined with Potassium, and that the precipitate consists of pure Iodide of Silver free from Bromide.

SILVER, SULPHURET OF.

Symbol, AgS. Atomic weight, 124.

This is a black compound, formed by the action of Sulphur upon metallic Silver, or of Sulphuretted Hydrogen, or Hydrosulphate of Ammonia, upon the Silver salts; the decomposition of Hyposulphite of Silver also furnishes the Black Sulphuret.

Sulphuret of Silver is insoluble in water, and also in those substances which dissolve the Chloride, Bromide, and Iodide, such as Ammonia, Hyposulphites, Cyanides, etc., but it dissolves in Nitric Acid, being converted into soluble Sulphate and Nitrate of Silver. (See page 375).

SILVER, NITRATE OF.

Symbol, $AgONO_5$. Atomic weight, 170.

The preparation and properties of this salt have been explained at page 15, Part I. The following particulars

may be given in addition. Nitrate of Silver crystallizes in white plates, which are anhydrous; they have a bitter and metallic taste, and are soluble in an equal weight of water at 60°, and half their weight at 212°: the addition of Nitric Acid to the water diminishes the solubility. Boiling Alcohol takes up one-fourth its weight of Nitrate of Silver, but deposits nearly the whole on cooling.

When heated in a crucible, Nitrate of Silver fuses, and at a higher temperature evolves Oxygen gas. The fused Nitrate dissolves in water, leaving a black powder, which is probably metallic Silver: the solution is alkaline to test-paper, and gives off red fumes of Peroxide of Nitrogen on the addition of Acetic Acid; it contains Nitrite of Silver, and also Oxide (possibly combined in the form of a *Sub*-Nitrite).

Solution of Nitrate of Silver is decomposed by metallic Iron, Zinc, Copper, Mercury, etc., with formation of a precipitate of metallic Silver, which is often beautifully crystalline.

SILVER, AMMONIO-NITRATE OF.

Crystallized Nitrate of Silver absorbs Ammoniacal gas rapidly, with production of heat sufficient to fuse the resulting compound, which is white, and consists of 100 parts of the Nitrate + 29·5 of Ammonia.

The compound however which Photographers employ, under the name of Ammonio-Nitrate of Silver, may be viewed more simply as a solution of the Oxide of Silver in Ammonia, without reference to any *salt* of Ammonia, such as the Nitrate, which may be associated with it.

For the preparation and properties of Ammonio-Nitrate of Silver, see pages 188 and 281.

SILVER, NITRITE OF.

Symbol, $AgO\,NO_3$. Atomic weight, 154.

The Nitrite of Silver is a compound of Nitrous Acid, or NO_3, with Oxide of Silver. It is formed by heating Nitrate of Silver, so as to drive off a portion of its Oxygen, or more conveniently, by mixing Nitrate of Silver and Nitrate of Potash in equal parts, fusing strongly, and dissolving in a small quantity of boiling water; on cooling, the Nitrite crystallizes out, and may be purified by pressing in blotting-paper. Mr. Hadow describes an economical method of preparing Nitrite of Silver in quantity, viz. by heating 1 part of Starch in 8 of Nitric Acid of 1·25 specific gravity, and conducting the evolved gases into a solution of pure Carbonate of Soda until all effervescence has ceased. The Nitrite of Soda thus formed is afterwards added to Nitrate of Silver in the usual way.

Properties.—Nitrite of Silver is soluble in 120 parts of cold water; easily soluble in boiling water, and crystallizes, on cooling, in long slender needles. It has a certain degree of affinity for Oxygen, and tends to pass into the condition of Nitrate of Silver; but it is probable that its Photographic qualities depend more upon a decomposition of the salt and liberation of Nitrous Acid.

Properties of Nitrous Acid.—This substance possesses very feeble acid properties, its salt being decomposed even by Acetic Acid. It is an unstable body, and splits up, in contact with water, into Binoxide of Nitrogen and Nitric Acid. The Peroxide of Nitrogen, NO_4, is also decomposed by water into Nitric Acid and Nitric Oxide or Binoxide of Nitrogen. (Page 320.)

SILVER, ACETATE OF.

Symbol, AgO ($C_4H_3O_3$). Atomic weight, 167.

This is a difficultly soluble salt, deposited in lamellar crystals when Acetic Acid is added to a strong solution of Nitrate of Silver. If the Acetic Acid be previously neutralized with Carbonate of Soda, the Acetate of Silver falls more readily, since the Nitric Acid which would otherwise be liberated and impede the decomposition, is united to a base.

Acetate of Soda + Nitrate of Silver
= Acetate of Silver + Nitrate of Soda.

SILVER, HYPOSULPHITE OF.

Symbol, AgO S_2O_2. Atomic weight, 164.

This salt is fully described in Part I. page 166 to 169. For the properties of the soluble double salt of Hyposulphite of Silver and Hyposulphite of Soda, see page 54.

SULPHURETTED HYDROGEN. *See* HYDROSULPHURIC ACID.

SULPHURIC ACID.

Symbol, SO_3. Atomic weight, 40.

Sulphuric Acid may be formed by oxidizing Sulphur with boiling Nitric Acid; but this plan would be too expensive to be adopted on a large scale. The commercial process for the manufacture of Sulphuric Acid is exceedingly ingenious and beautiful, but it involves reactions which are somewhat complicated, and do not admit of a superficial explanation. The Sulphur is first burnt into gaseous Sulphurous Acid (SO_2), and then by the agency of Binoxide of Nitrogen gas, an additional atom of Oxygen

is imparted from the atmosphere, so as to convert the SO_2 into SO_3, or Sulphuric Acid.

Properties.—Anhydrous Sulphuric Acid is a white crystalline solid. The strongest liquid acid always contains one atom of water, which is closely associated with it, and cannot be driven off by the application of heat.

This *mono-hydrated* Sulphuric Acid, represented by the formula $HO\ SO_3$, is a dense fluid, having a specific gravity of about 1·845; boils at 620°, and distils without decomposition. It is not volatile at common temperatures, and therefore does not *fume* in the same manner as Nitric or Hydrochloric Acids. The concentrated acid may be cooled down even to zero without solidifying; but a weaker compound, containing twice the quantity of water, and termed *glacial* Sulphuric Acid, crystallizes at 40° Fahr. Sulphuric Acid is intensely acid and caustic, but it does not destroy the skin or dissolve metals so readily as Nitric Acid (see page 16). It has an energetic attraction for water (page 86), and when the two are mixed, condensation ensues, and much heat is evolved; four parts of acid and one of water produce a temperature equal to that of boiling water. Mixed with aqueous Nitric Acid, it forms the compound known as Nitro-Sulphuric Acid, and described at pages 86 and 209.

Sulphuric Acid possesses intense chemical powers, and displaces the greater number of ordinary acids from their salts (page 316). It *chars* organic substances, by removing the elements of water, and converts Alcohol into Ether in a similar manner. The *strength* of a given sample of Sulphuric Acid may generally be calculated from its specific gravity, and a Table is given by Dr. Ure for that purpose. (See Appendix.)

Impurities of Commercial Sulphuric Acid.—The liquid acid sold as Oil of Vitriol is tolerably constant in composition, and seems to be as well adapted for Photogra-

phic use as the pure Sulphuric Acid, which is far more expensive. The specific gravity should be about 1·836 at 60°. If a drop, evaporated upon Platinum foil, gives a fixed residue, probably Bisulphate of Potash is present. A milkiness, on dilution, indicates Sulphate of Lead. (See page 210.)

Test for Sulphuric Acid, either free or in combination with bases.—If the presence of Sulphuric Acid, or soluble Sulphate, is suspected in any liquid, it is tested for by adding a few drops of a dilute solution of Chloride of Barium, or Nitrate of Baryta. A white precipitate, *insoluble in Nitric Acid*, indicates Sulphuric Acid. If the liquid to be tested is very acid, from Nitric or Hydrochloric Acids, it must be largely diluted before testing, or a crystalline precipitate will form, caused by the sparing solubility of the Chloride of Barium itself in acid solutions.

SULPHUROUS ACID.

Symbol, SO_2. Atomic weight, 32.

This is a gaseous compound, formed by burning Sulphur in atmospheric air or Oxygen gas; also by heating Oil of Vitriol in contact with metallic Copper, or with Charcoal.

When an acid of any kind is added to Hyposulphite of Soda, Sulphurous Acid is formed as a product of the decomposition of Hyposulphurous Acid, but it afterwards disappears from the liquid by a secondary reaction, resulting in the production of alkaline Polythionates. (See pages 162 and 165.)

Properties.—Sulphurous Acid possesses a peculiar and suffocating odour, familiar to all in the fumes of burning Sulphur. It is a feeble acid, and escapes with efferves-

cence, like Carbonic Acid, when its salts are treated with Oil of Vitriol. It is soluble in water.

TETRATHIONIC ACID.

Symbol, S_4O_5. Atomic weight, 104.

The chemistry of the Polythionic Acids and their salts will be found carefully described in the first part of this Work, pages 163 to 166.

WATER.

Symbol, HO. Atomic weight, 9.

Water is an Oxide of Hydrogen, containing single atoms of each of the gases.

Distilled water is water which has been vaporized and again condensed; by this means it is freed from earthy and saline impurities, which are not volatile, and hence remain behind in the body of the retort. Pure water leaves no residue on evaporation, and should remain perfectly clear on the addition of Nitrate of Silver; also it should be neutral to test-paper.

Impurities of common Water.—Hard water, as it is termed, usually contains Sulphate of Lime, and Carbonate of Lime dissolved in Carbonic Acid, also Chloride of Sodium in greater or less quantity. On boiling the water, the Carbonic Acid gas is evolved, and the greater part of the Carbonate of Lime (if any is present) deposits, and forms an earthy incrustation on the boiler.

In testing water for Sulphates and Chlorides, acidify a portion with a few drops of *pure* Nitric Acid, free from Chlorine; then divide it into two parts, and add to the first Chloride of Barium, and to the second Nitrate of Silver—a milkiness, in either case, indicates the presence of impurity. The *Photographic Nitrate Bath* cannot be

used as a test for Chlorides, since the Iodide of Silver it contains is precipitated on dilution.

Rain water, having already undergone a natural process of distillation, is free from inorganic salts if collected in clean vessels; but it usually contains a minute portion of *Ammonia* (page 267), and often organic matter, which tinges it of a brown colour.

APPENDIX.

QUANTITATIVE TESTING OF SOLUTIONS OF NITRATE OF SILVER.

THE amount of Nitrate of Silver contained in solutions of that salt, may be estimated with sufficient delicacy for ordinary Photographic operations by the following simple process.

Take the *pure* crystallized Chloride of Sodium, and either dry it strongly or fuse it at a moderate heat, in order to drive off any water which may be retained between the interstices of the crystals; then dissolve in distilled water, in the proportion of 8½ grains to 6 fluid ounces.

In this way, a standard solution of salt is formed, each drachm of which (containing slightly more than one-sixth of a grain of salt) will precipitate exactly half a grain of Nitrate of Silver.

In order to use it, measure out exactly one drachm of the Bath in a minim measure and place it in a two-ounce stoppered phial, taking care to rinse out the measure with a drachm of distilled water, which is to be added to the former; then pour in the salt solution, in the proportion of a drachm for every 4 grains of Nitrate *known to be present* in an ounce of the Bath which is to be tested; shake the contents of the bottle briskly, until the white curds are perfectly separated, and the supernatant liquid is clear and colourless; then add fresh portions of the standard solution, by 30 minims at a time, with constant shaking. When the last addition causes no *milkiness*, read off the total number of drachms employed (the last half-drachm being subtracted),

and multiply that number by 4 for the weight in grains of the Nitrate of Silver present in an ounce of the Bath.

In this manner the strength of the Bath is indicated within two grains to the ounce, or even to a single grain if the last additions of standard salt-solution be made in portions of 15, instead of 30 minims.

Supposing the Bath to be tested is thought to contain about 35 grains of Nitrate to the ounce, it will be convenient to begin by adding to the measured drachm, 7 *drachms* of the standard solution; afterwards, as the milkiness and precipitation become less marked, the process must be carried on more cautiously, and the bottle shaken violently for several minutes, in order to obtain a clear solution. A few drops of Nitric Acid added to the Nitrate of Silver facilitate the deposition of the Chloride; but care must be taken that the sample of Nitric Acid employed is pure and free from Chlorine, the presence of which would cause an error.

RECOVERY OF SILVER FROM WASTE SOLUTIONS,—FROM THE BLACK DEPOSIT OF HYPO BATHS, ETC.

The manner of separating metallic Silver from old solutions varies according to the presence or absence of alkaline Hyposulphites and Cyanides.

a. *Separation of metallic Silver from old Nitrate Baths.*—The Silver contained in solutions of the Nitrate, Acetate, etc., may easily be precipitated by suspending a strip of sheet Copper in the liquid; the action is completed in two or three days, the whole of the Nitric Acid and Oxygen passing to the Copper, and forming a blue solution of the Nitrate of Copper. The metallic Silver however separated in this manner, always contains a portion of Copper, and gives a blue solution when dissolved in Nitric Acid.

A better process is to commence by precipitating the Silver entirely in the form of *Chloride of Silver*, by adding common Salt until no further milkiness can be produced. If the liquid is well stirred, the Chloride of Silver sinks to the bottom, and may be washed by repeatedly filling the vessel with common water, and pouring off the upper clear portion when the clots have

again settled down. The Chloride of Silver thus formed may afterwards be reduced to metallic Silver by a process which will presently be described.

b. *Separation of Silver from solutions containing alkaline Hyposulphites, Cyanides, and Iodides.*—In this case the Silver cannot be precipitated by adding Chloride of Sodium, since the Chloride of Silver is *soluble* in such liquids. Therefore it is necessary to use the Sulphuretted Hydrogen, or the Hydrosulphate of Ammonia, and to separate the Silver in the form of *Sulphuret.*

Sulphuretted Hydrogen gas is readily prepared, by fitting a cork and flexible tubing to the neck of a pint bottle, and having introduced *Sulphuret of Iron* (sold by operative chemists for the purpose), about as much as will stand in the palm of the hand, pouring upon it 1½ fluid ounce of Oil of Vitriol diluted with 10 ounces of water. The gas is generated gradually without the application of heat, and must be allowed to bubble up through the liquid from which the Silver is to be separated. The smell of Sulphuretted Hydrogen being offensive, and highly poisonous if inhaled in a concentrated form, the operation must be carried on in the open air, or in a place where the fumes may escape without doing injury.

When the liquid begins to acquire a strong and persistent odour of Sulphuretted Hydrogen, the precipitation of Sulphuret is completed. The black mass must therefore be collected upon a filter, and washed by pouring water over it, until the liquid which runs through gives little or no precipitate with a drop of Nitrate of Silver.

Conversion of Sulphuret of Silver into metallic Silver.—The black Sulphuret of Silver may be reduced to the state of metal by roasting and subsequent fusion with Carbonate of Soda; but it is more convenient, in operating on a small scale, to proceed in the following manner:—first convert the Sulphuret into Nitrate of Silver, by boiling with Nitric Acid diluted with two parts of water; when all evolution of red fumes has ceased, the liquid may be diluted, allowed to cool, and filtered from the insoluble portion, which consists principally of Sulphur, but also contains a mixture of Chloride and Sulphuret of Silver, unless the Nitric Acid employed was free from Chlorine; it may

be heated in order to volatilize the Sulphur, and then digested with Hyposulphite of Soda, or added to the Hypo Bath.

The solution of Nitrate of Silver obtained by dissolving Sulphuret of Silver is always strongly acid with Nitric Acid, and also contains *Sulphate* of Silver. It may be crystallized by evaporation; but unless the quantity of material operated on is large, it will be better to precipitate the Silver in the form of Chloride, by adding common Salt, as already recommended.

REDUCTION OF CHLORIDE OF SILVER TO THE METALLIC STATE.

The Chloride of Silver is first to be carefully washed, by filling up the vessel which contains it, many times, with water, and pouring off the liquid, or drawing it off close with a siphon. It may then be dried at a gentle heat, and fused with twice its weight of dry Carbonate of Potash, or, better still, with a mixture of the Carbonates of Potash and Soda.

The process for reducing Chloride of Silver in the moist way, by metallic Zinc and Sulphuric Acid, is more economical and less troublesome than that just given; it is conducted as follows:—The Chloride, after having been well washed as before, is poured out into a large flat dish, and a bar of metallic Zinc placed in contact with it. A small quantity of Oil of Vitriol, diluted with four parts of water, is then added, until a slight effervescence of Hydrogen gas is seen to take place. The vessel is set aside for two or three days, and is not to be disturbed, either by stirring or by moving the bar. The reduction begins with the Chloride immediately in contact with the Zinc, and afterwards radiates in all directions. When the whole mass has become of a grey colour, the bar is to be carefully removed and the adhering Silver washed off with a stream of water; the Zinc usually presents a honeycomb appearance, with irregularities upon the surface, which however are not metallic Silver;—they consist only of Zinc or of Oxide of Zinc.

In order to ensure the purity of the Silver, a fresh addition of Sulphuric Acid must be made, after the Zinc bar has been removed, and the digestion continued for several hours, in order to dissolve any fragments of metallic Zinc which may have been

inadvertently detached. The grey powder is then to be washed repeatedly with water, until the liquid which runs off gives no precipitate with Carbonate of Soda, and may be converted into Nitrate of Silver by boiling with Nitric Acid diluted with two parts of water.

SEPARATION OF GOLD FROM THE BLACK POWDER DEPOSITED IN HYPO COLOURING BATHS PREPARED WITH CHLORIDE OF GOLD.

In this case the black deposit consists of a mixture of the Sulphurets of Gold and Silver. They may be separated by boiling, first, with pure Nitric Acid diluted with two parts of water, in order to extract the greater part of the Silver, and afterwards with Aqua-regia (see page 359), which takes up the Gold, and leaves any Silver which may still be present, in the form of insoluble Chloride of Silver.

The Aqua-regia solution of Gold may be evaporated on a water Bath until it reaches a syrupy consistence, or the Gold may be precipitated from it in the metallic form by diluting with water and adding a sufficient quantity of Protosulphate of Iron.

ON FILTRATION AND WASHING PRECIPITATES.

In preparing filters cut the paper into squares of a sufficient size, and fold each square neatly upon itself, first into a half-square, and then again, at right angles, into a quarter-square;—round off the corners with a pair of scissors, and open out the filter into a conical form, when it will be found to drop exactly into the funnel and to be uniformly supported throughout.

Before pouring in the liquid, always moisten the filter with distilled water, in order to expand the fibres; if this precaution is neglected, the pores are apt to become choked in filtering liquids which contain finely divided matter in suspension. The solution to be filtered may be poured gently down a glass rod, held in the left hand, and directed against the side of the funnel, near to the upper part. If it does not immediately run clear, it will usually do so on returning it into the filter and allowing it to pass through a second time.

Mode of washing precipitates.—Collect the precipitate upon a

filter and drain off as much of the mother-liquor as possible; then pour in distilled water by small portions at a time, allowing each to percolate through the deposit before adding a fresh quantity. When the water passes through perfectly pure, the washing is complete; in testing it, a single drop may be laid upon a strip of glass and allowed to evaporate spontaneously in a warm place, or the proper chemical reagents may be applied, and the washing continued until no impurity can be detected. Thus, for example, in washing the Sulphuret of Silver precipitated from a Hypo Bath by means of Hydrosulphate of Ammonia, the process will be completed when the water which runs through causes no deposit with a drop of Nitrate of Silver solution.

ON THE USE OF TEST-PAPERS.

The nature of the colouring matter which is employed in the preparation of Litmus-paper has already been described at page 355.

In testing for the alkalies and basic oxides generally, the blue litmus-paper which has been reddened by an acid may be used, or, in place of it, the *turmeric* paper. Turmeric is a yellow vegetable substance which possesses the property of becoming brown when treated with an alkali; it is however decidedly less sensitive than the reddened litmus, and is scarcely affected by the weaker bases, such as Oxide of Silver.

In using test-papers observe the following precautions:—they should be kept in a dark place, and protected from the action of the air, or they soon become purple from Carbonic Acid, always present in the atmosphere in small quantity. By immersion in water containing about one drop of Liquor Potassæ in four ounces, the blue colour is restored.

Test-papers prepared with *porous* paper show the red colour better than those upon glazed or strongly sized paper. If the quantity of acid present however is small, it is not sufficient in any case simply to dip the paper in the liquid; a small strip should be thrown in, and allowed to remain for ten minutes or a quarter of an hour.

If the paper, on immersion, assumes a *wine-red* or purple tint, in place of a decided red, it is probably caused by Carbonic

Acid gas: in that case the blue colour returns when the paper is washed and held to the fire.

Blue litmus-papers may be changed to the red papers used for alkalies by soaking in water acidified with Sulphuric Acid, one drop to half a pint.

REMOVAL OF SILVER STAINS FROM THE HANDS, LINEN, ETC.

The black stains upon the hands caused by Nitrate of Silver, may readily be removed by moistening them and rubbing with a lump of Cyanide of Potassium. As this salt however is highly poisonous, many may prefer the following plan:—wet the spot with a saturated solution of Iodide of Potassium, and afterwards with Nitric Acid; the strong Nitric Acid acts upon the skin and turns it yellow, it must therefore be diluted with two parts of water before use.

Stains upon white linen may be easily removed by brushing them with a solution of Iodine in Iodide of Potassium, and afterwards washing with water and soaking in Hyposulphite of Soda, or Cyanide of Potassium, until the yellow Iodide of Silver is dissolved out; the Bichloride of Mercury (neutral solution) also answers well in many cases.

A TABLE SHOWING THE QUANTITY OF ANHYDROUS ACID IN DILUTE SULPHURIC ACID OF DIFFERENT SPECIFIC GRAVITIES. (URE.)

Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.
1·8485	81·54	1·8115	73·39	1·7120	65·23
1·8475	80·72	1·8043	72·57	1·6993	64·42
1·8460	79·90	1·7962	71·75	1·6870	63·60
1·8439	79·09	1·7870	70·94	1·6750	62·78
1·8410	78·28	1·7774	70·12	1·6630	61·97
1·8376	77·46	1·7673	69·31	1·6520	61·15
1·8336	76·65	1·7570	68·49	1·6415	60·34
1·8290	75·83	1·7465	67·68	1·6321	59·52
1·8233	75·02	1·7360	66·86	1·6204	58·71
1·8179	74·20	1·7245	66·05	1·6090	57·89

A TABLE SHOWING THE QUANTITY OF ANHYDROUS ACID IN THE LIQUID NITRIC ACID OF DIFFERENT SPECIFIC GRAVITIES. (URE.)

Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.
1·5000	79·700	1·4730	71·730	1·4385	63·760
1·4980	78·903	1·4700	70·933	1·4346	62·963
1·4960	78·106	1·4670	70·136	1·4306	62·166
1·4940	77·309	1·4640	69·339	1·4269	61·369
1·4910	76·512	1·4600	68·542	1·4228	60·572
1·4880	75·715	1·4570	67·745	1·4189	59·775
1·4850	74·918	1·4530	66·948	1·4147	58·978
1·4820	74·121	1·4500	66·155	1·4107	58·181
1·4790	73·324	1·4460	65·354	1·4065	57·384
1·4760	72·527	1·4424	64·557	1·4023	56·587

WEIGHTS AND MEASURES.

Troy or Apothecaries' Weight.

1 Pound = 12 Ounces. 1 Ounce = 8 Drachms. 1 Drachm = 3 Scruples. 1 Scruple = 20 grains. (1 Ounce Troy = 480 grains.)

Avoirdupois Weight.

1 Pound = 16 Ounces. 1 Ounce = 16 Drachms. 1 Drachm = 27·343 grains. (1 Ounce Avoirdupois = 437·5 grains.)

Imperial Measure.

1 gallon = 8 Pints. 1 Pint = 20 Ounces. 1 Ounce = 8 Drachms. 1 Drachm = 60 Minims. (1 Fluid Ounce of water *weighs* 437·5 grains, or 1 Ounce Avoirdupois.)

French Measures of Weight.

1 Gramme = 15·444 English Grains.

INDEX.

Aberration, chromatic, 71; spherical, 74.
Acids, nature of, 310.
Accelerating agents, 116.
Actinism explained, 62.
Action of Light upon Iodide of Silver, hypotheses on, 123.
Affinity, chemical, 315.
Albumen, preparation of Positive paper with, 278.
Alcohol, purification of, 221.
Alkalies, nature of, 310.
Amber varnish, 262.
Ammonio-Nitrate of Silver, its Photographic action, 188; preparation of, 281.
Atomic weights, 326.

Bichloride of Mercury, whitening process by, 147; solution for, 241.
Blackening Negatives, 155.
Bromide of Silver, its Photographic peculiarities, 193.

Calotype, explanation of term, 12.
Camera, theory of construction of, 70; mode of testing accuracy of, 263.
Chemical affinity, illustrations of, 315.
Chemical spectrum, 193.
Chemical focus, directions for finding, 263; relation to visual focus, 79.
Chemical elements, 307.
Chloride of Silver, its Photographic action, 24; theory of preparation of sensitive layer of, 30.
Chromatic aberration, 71.
Chloride of Gold, for colouring Baths, theory of, 180; preparation of, 285.
Cleaning glass plates, 249.
Collodion, its physical properties, 92; Iodized, chemistry of, 96; manufacture of, 207; Positive, formula for, 232; Negative, formula for, 245; renovation of deteriorated, 101; mode of coating glasses with, 251.
Collodio-Iodide of Silver, its physical properties, 107; its Photographic action, 110; sensitiveness of, causes affecting, 111; development of, conditions influencing, 118; excessive sensitiveness of, explained, 127.
Colours, chemical action on sensitive film, 61.
Coloured objects, mode of copying, 196.
Colouring of Positive proofs, circumstances which affect, 174.

Combination of elements, 309; laws of, 325.
Cyanide of Potassium, theory of its action, 55; preparation of solution of, 248.

Daguerreotype, chemistry of the, 197.
Development of an invisible image, explanation of, 35; of Collodio-Iodide of Silver, causes influencing, 118; of Negatives, theory of, 151; of Positives, details of, 257; of Negatives, details of, 259.
Developing agents, their chemistry sketched, 39; for Positives, preparation of, 239; for Negatives, preparation of, 247.
Double decomposition, 317.

Elementary bodies, table of, 307.
Elements, combination of, 30
Equivalent proportions, 323.
Ether, purification of, 219.
Experiments illustrating action of Light upon Chloride of Silver, 31.
Exposure in the Camera, 255.

Film, Collodio-Iodide, its physical properties, 107.
Filters, mode of cutting, 377.
Fixing the image, theory of, 50; Alkaline Chlorides and Iodides, employed for, 52; Alkaline Hyposulphites and Cyanides employed for, 53.
Fixing and colouring Baths, chemistry of, 169; Photographic action of, 177; addition of Gold salt to, 180; details of preparation of, 283.
Fixing solutions for Collodion Photographs, 248.
Fogging, theory of, 135; mode of obviating, 265.
Focussing the object, 256.
Foci, actinic and luminous, 79; actinic, mode of finding, 263.
Foliage, copying, 196.
Formulæ for solutions required in Collodion process, 233.

Gallic Acid, peculiarities as a developer, 120.
Gallo-Nitrate of Silver, 116.
Glass plates, cleaning, 249; coating with Collodion, 253.
Gold, Chloride of, preparation of colouring Bath with, 285.
Gold, Hyposulphite of, theory of its colouring action, 180.
Gradation of tone, circumstances affecting, 129.
Gun-cotton, preparation of, 207.

Historical sketch of Photography, 8.
Honey process of Mr. Shadbolt, 301.
Hyposulphite of Soda, theory of its fixing action, 54; its decomposition by acids, 161.
Hypo Bath for fixing Negatives, 248; for fixing and colouring Positives, 283.

Imperfections in Collodion Photographs, 265; in Positives, 273; in Negatives, 272.
Intensity, explanation of term, 111.
Iodine, preparation of colouring Bath by, 284.
Iodides, retarding effect upon colouring Bath, 182.
Iodide of Potassium, purification of, 222.
Iodide of Ammonium, preparation of, 223.
Iodide of Iron, preparation of, 224.
Iodide of Potassium and Silver, preparation of, 224.

Iodide of Silver, hypotheses of action of light on, 123; its reduction by developer explained, 46.
Iodized Collodion, chemistry of, 96; formulæ for, 232.

Latent Image, development of, its theory, 35.
Lenses, forms of, 66; decomposition of Light by, explained, 67; foci of, 68, formation of Images by, 69; use of stops on, 76; portrait, 77; chemical foci of, 79.
Light, its action upon Silver Salts, 24; experiments illustrating, 31; its compound nature, 57; its properties, 60; refraction of, 63; action on Iodide of Silver, hypotheses on, 123.
Light, yellow, its nature shown, 62.

Manipulations of Collodion process, 249.
Manipulations of Photographic Printing, 289.
Markings on Collodion Pictures, 271.
Measures and weights, 380.

Negatives, theory of processes for, 150; theory of development, 151; details of development, 259; varnishes for, 262; formulæ for, 242.
Nitric Acid, its oxidizing powers, 15; its effect upon the sensitiveness, 114; upon the development, 121; table of strength of, 380.
Nitrate of Silver, Photographic action of, 24; solubility of Iodide of Silver in, 101.
Nitrate Bath, 101; decomposition by Light, 102; acidity of, 103; alkalinity of, 105; preparation of, 225; formulæ for, 246; quantitative testing of, 373.
Nitrate of Magnesia process, 298.
Nitrite of Silver affects sensitiveness, 116; affects development, 122; produces fogging, 136; solarizes the plate, 146.
Nomenclature, chemical, 318.
Notation, chemical, 321.

Organic bodies, chemistry of, 328.

Paper, Photographic, selection of, 277.
Perchloride of Iron, preparation of
colouring Bath wit
Photography, historic
8.
Photographic action
Silver, 23; of Coll
Silver, 110; of H
Bath, 172.
Photographic proces
resemblance betwe
ing, theory of, 15
Portraits, lenses for
for, 196; directio
256.
Positives, direct, t
cesses for, 141; e
Negatives, 155; f
lutions for, 232;
for, 249; backing
Positives on paper, t
processes for, 276
Practice of Collodio
Printing, Photograp
159; practice of,
Prismatic spectrum,
Protonitrate of Iro
of, 231.
Pyrogallic Acid, to de
sitives, 145; Negatives, 155.
Pyroxyline, its chemistry, 84; its preparation, 207.

Reduction of Metallic Oxides, theory of, 37; Silver Salts, theory of, 42; practical details of, 375.
Salts, nature of, 312.
Salts of Silver, their Photographic action, 23; theory of their reduction by developer, 42; directions for obtaining metal from, 374.
Sensitiveness, term explained, 111.
Sensitiveness of Collodion film, causes influencing, 111; explained, 127; preservation of, 296.
Sensitive surfaces, general theory of, 28.
Sensitive paper, theory of prepa- ... of prepara- ... Ammonio-Ni- ... in Nitrate ... ering from ... 374; reduction from Chloride, 376; stains, removal of, 379.
Solar spectrum, 58.
Spherical aberration, 74.
Spots on Collodion plates, 269.
Stains, Silver, removal of, 379.
Standard acid solution, preparation of, 228.
Stops, use of, 76.
Strength of acids, tables of, 379.
Sulphuric Acid, table of strength of, 379.
Sulphate of Quinine, absorption of rays by, 194.
Syruped Collodion film, 301.
Symbols, use of, 321.

Test-papers, use of, 378.

Varnishes for Collodion Photographs, 262.

Weights and Measures, table of, 380.

JOHN EDWARD TAYLOR, PRINTER,
LITTLE QUEEN STREET, LINCOLN'S INN FIELDS.

00034100

Digitized with financial assistance from the
Government of Maharashtra
on 23 March, 2016